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ERRATUM

Analytica Chimica Acta, 20 (1959) 140.

Table 1, on top of page 140: subheadings of columms: Instead of "2 ml of 1.0% solution" and "2 ml of 5.0% solution" read "2 ml of 0.1% solution" and "2 ml of 0.5% solution".

The subheadings of the lower part of Table I are correct.

A PRECISE MICROHETEROMETRIC DETERMINATION OF BISMUTH AS IODIDE WITH PYRAMIDON

A STUDY OF THE REACTION AND OF THE COMPOUNDS

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INTRODUCTION

Bismuth can be determined in the presence of potassium iodide by precipitation with alkaloids. Conversely, alkaloids can also be precipitated by the soluble bismuth iodide anion complex. The composition of the insoluble compound generally cited in the literature is $RN.BiI_4$. Analogous insoluble compounds are also obtained with the CNS^- ion instead of iodide. The use of this kind of compound for analytical purposes is very extensive[1]. Although the reactions concerned are very sensitive, they do not allow the determination of traces of metals in the presence of very large excesses of foreign metals. In addition, the insoluble compounds obtained are often influenced by foreign neutral salts present and the latter may even entirely prevent their precipitation. Some twenty years ago, SPACU and co-workers, as well as many other investigators, studied these compounds and their analytical applications extensively. Since then many organic reagents with specific properties have been found, and these are preferred to the above-mentioned methods. Although much work was carried out on the iodide and thiocyanate methods, the published information suffers from an excess of empirical detail and lacks a deeper insight into the formation and the structure of the compounds obtained. It is scarcely possible that these very insoluble compounds have structures as simple as presented for them in the literature.

The results of our studies are not limited to pyramidon, but concern many other complicated heterocyclic nitrogen compounds such as the alkaloids, etc., all of which act on the same basis.

Our aim was to make a more thorough investigation of the reactions concerned, to study the working conditions and to determine the various intermediate and final compounds which appear in the system. The following conclusions were reached as a result of our study: the reactions of iodo-complexes are very sensitive and specific for the determination of traces of certain metals, especially bismuth and mercury. The reactions always proceed quickly and the heterometric end-points obtained are accurate and unambiguous. The error was negligible, and the sensitivity of the reaction studied was of the same order of magnitude as with diethyldithiocarbamate[2-5].

As to the compounds which were obtained from the three components, their compositions depended on which of the components was used as titrant. Altogether more than ten compounds were traced and four final compounds were found. Each of these four could be used for the determination both of bismuth and of pyramidon.

Our investigation is being continued, and we are now testing different alkaloids as to the sensitivity and precision of their determination with a standard bismuth solution. The method may be of special interest for the determination of alkaloids, as in this case the question of interference by metals does not exist.

EXPERIMENTAL

The same apparatus and the same experimental conditions were observed as in previous heterometric investigations[2-5]. All titrations were carried out using a red filter. The reaction temperature was always 20°. The following reagents were used:

Pyramidon, Ph H, Dubeck and Dolder. A $0.02M$ stock solution was prepared in water and kept in a brown bottle in an ice box. More dilute solutions were obtained by diluting with water. These solutions were freshly prepared every three days. The $0.00125M$ solution was prepared twice a day.

Bismuth nitrate, $Bi(NO_3)_3 \cdot 5H_2O$, Baker's Analyzed. A stock solution of $0.05M$ was prepared by weighing the salt and diluting in nitric acid. The solution obtained was $1N$ in nitric acid. More dilute solutions were prepared from the stock solution and acidified water, so that in the final solutions the molar concentration of the nitric acid was twenty-two times that of the bismuth.

Potassium iodide, Baker's Analyzed. A $0.5M$ stock solution was prepared, from which more dilute solutions were always freshly prepared. All solutions were kept in dark brown bottles.

RESULTS

Many titrations were carried out in which either solutions of bismuth nitrate, or pyramidon, or potassium iodide were titrated into solutions containing the other two components. A selection of such experiments is compiled in three tables, while the courses of some titrations are presented in the figures. (The numeration is the same in the tables and in the figures.) It was found that the most suitable concentration for the analysis of bismuth was $\sim 0.0005M$ Bi. The same molar concentration was suitable for the determination of pyramidon. The concentration of potassium iodide in solution was not critical and there was no upper limit to its concentration. The concentration of potassium iodide in the titrated solution was $0.02M$, but a $0.01M$ solution was sufficient. The molar ratio of bismuth to iodide was therefore 1 :40, and in some cases 1:20. The minimum amount of potassium iodide which was necessary for the reaction was found from titrations with potassium iodide as titrant. Evidently all three components acted stoichiometrically in all titrations. A minimum amount of nitric acid was also necessary to counteract the hydrolysis of bismuth. On the other hand, if more nitric acid was used, the sensitivity of the reaction was reduced and the end-point was no longer certain (see Table I, Expts. 13–15).

Pyramidon as titrant

In the absence of foreign metals

The compositions of the experiments and the results obtained are compiled in Table I and in Fig. 1. From the table the influence of neutral salts, various anions and halogenides can be seen.

Composition of precipitates. In almost all cases, heterometric curves with a critical maximum optical density point followed by a horizontal line were obtained. The critical point always occurred exactly at the molar ratio of 1 [Bi]:1 [Py]. (The critical point was obtained at the intersection of the last part of the reaction curve with the horizontal line.) The error was mostly close to zero.

Supplements. The reaction studied was in general sensitive towards supplements and their amount was, therefore, restricted. In Table I the amounts cited are those which permitted the measurement of satisfactory titration curves. It was found that on the addition of small amounts of alcohol ($\leqslant$ 25–30%) the titration curve was steeper and the fixation of the end-point was generally easier. Therefore many titrations were repeated with some added alcohol. However, in a 50% alcohol solution (Expt. 5) no precipitation occurred at all. When the nitric acid was replaced by acetic acid (even in larger amount) the densities obtained were lower and no definite end-point was obtained. Acetic acid added to nitric acid had little influence (Expts. 17 and 18). The curve was also uninfluenced by moderate amounts of tartaric or citric acid added to the nitric acid (Expts. 29 and 31). However, in the presence of alcohol, citric and tartaric acid prevented precipitation (Expts. 30 and 32). Moderate amounts of orthophosphoric acid acted similarly to citric acid. But in the presence of larger amounts of phosphoric acid (0.5 ml M H_3PO_4) (Expts. 35–36) a *new final* critical point appeared at the molar ratio of 3 [Bi]:2 [Py]. As will be seen later, this point appeared in most of the regular titrations, but only as an *intermediate* point, further addition of Py

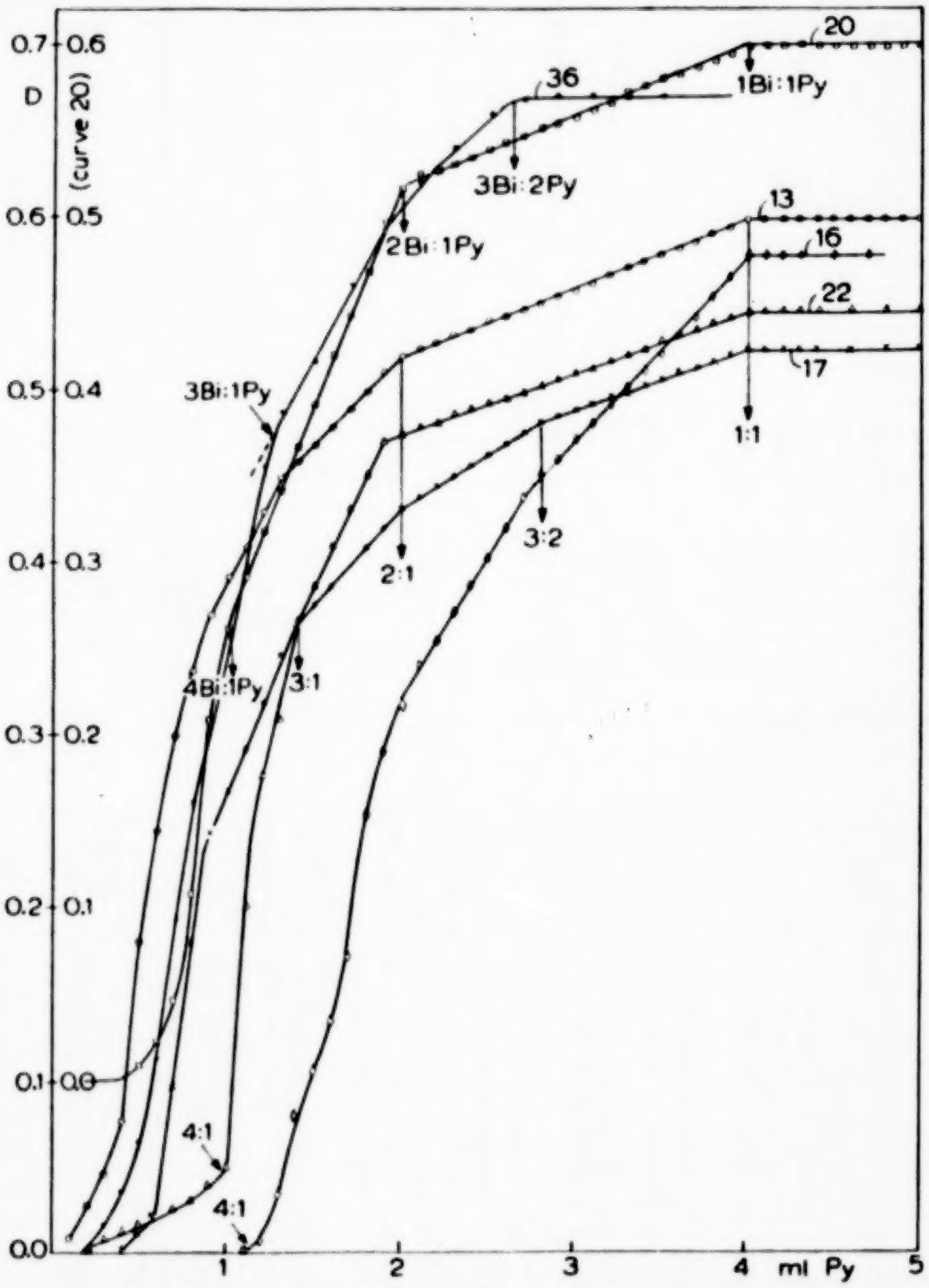

Fig. 1. Titrations of solutions of bismuth nitrate with pyramidon.

References p. 15

TABLE I

Composition: *a* ml $Bi(NO_3)_3$ + *b* ml KI + *c* ml supplements + water ad. 10 ml + *x* ml 0.00125*M* pyramidon (= titrant). Temp. = 20°. Fisher red filter.

Expt.	Composition	Found					Remarks
		Initial ppt. at ml	ml titrant at first max. p.	Max. optical density value	Titration time in min	% error	
1.	4 ml 0.001*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.05*M* KI	0.2	i 3.1 h	0.658	10	3.2	
2.	4 ml 0.001*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.1*M* KI	0.4	i 3.20 h	0.565	12	0.0	
3.	4 ml 0.001*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.05*M* KI + 3 ml alcohol	0.9	i 3.20 h	0.668	11	0.0	
4.	4 ml 0.001*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.1 *M* KI + 3 ml alcohol	1.0	i 3.20 h	0.668	10	0.0	
5.	2 ml 0.002*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.1 *M* KI + 5 ml alcohol						no ppt.
6.	4 ml 0.001*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.3 *M* KI	2.6	3.3(?)h	0.163	11		
7.	4 ml 0.001*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.05*M* KI + 1 ml alcohol	0.1	i 3.20 h	0.745	11	0.0	i.i.p. 1.8
8.	4 ml 0.001*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.05*M* KI + 1 ml 0.1*M* NaCl	0.8	?	0.29	10		end-point uncertain
9.	4 ml 0.001*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.05*M* KI + 1 ml 0.1*M* KBr	1.0	?	0.17	11		end-point uncertain
10.	4 ml 0.001*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.05*M* KI + 2 ml 2*M* NH_4NO_3		?	0.09			
11.	4 ml 0.001*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.05*M* KI + 1 ml 0.5*M* $(NH_4)_2SO_4$		?	0.05			
12.	4 ml 0.001*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.05*M* KI + 2 ml *M* acetic acid	0.6	i 3.20 h	0.412	10	0.0	
13.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.1*M* KI	0.2	i 4.02 h	0.598	12	0.5	
14.	4 ml 0.00125*M* Bi + 3 ml *M* HNO_3 + 2 ml 0.1*M* KI	1.2	i 4.05 m	0.414	14	1.2	maximum point, then decrease
15.	4 ml 0.00125*M* Bi + 1.5 ml 2*M* HNO_3 + 0.4 ml 0.5*M* KI + 3 ml alcohol	$\sim$2.5	i 4.00 h	0.414	14	0.0	
16.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.1*M* KI + 3 ml alcohol	0.3	i 4.00 h	0.577	12	0.0	
17.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.1*M* KI + 2 ml *M* acetic acid	0.6	i 4.00 h	0.523	13	0.0	
18.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 0.4 ml 0.5*M* KI + 1 ml 2*M* acetic acid + 3 ml alc.	1.7	i 4.00 h	0.553	12	0.0	
19.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 0.4 ml 0.5*M* KI + 5 ml alcohol						no ppt.
20.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.1*M* KI + 0.5 ml *M* $(NH_4)_2SO_4$	0.6	i 4.02 h	0.598	12	0.5	

21.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 0.4 ml 0.5*M* KI + 0.5 ml *M* $(NH_4)_2SO_4$ + 3 ml alcohol	2.3	i 4.00 h	0.475	12	0.0	
22.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.1*M* KI + 1 ml *M* NH_4NO_3	0.4	i 4.00 h	0.545	14	0.0	i.i.p. 2.1
23.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 0.4 ml 0.5*M* KI + 1 ml 0.1*M* $(NH_4)_2SO_4$ + 3 ml alcohol	1.8	i 4.00 h	0.673	13	0.0	i.i.p. 2.6 and 3.4
24.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.1*M* KI + 1 ml 0.1*M* NaCl	0.4	i 4.00 h	0.648	12	0.0	
25.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 0.4 ml 0.5*M* KI + 1 ml 0.1*M* NaCl + 3 ml alcohol	1.6	i 4.00 h	0.485	13	0.0	
26.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.1*M* KI + 1 ml 0.1*M* KBr	1.0	i 4.00 h	0.420	12	0.0	
27.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 0.4 ml 0.5*M* KI + 1 ml 0.1*M* KBr + 3 ml alc.			0.097			
28.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 0.4 ml 0.5*M* KI + 1 ml 0.05*M* KBr + 3 ml alc.	2	i 3.95 h	0.456	13	1.2	
29.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.1*M* KI + 3 ml 0.1*M* tartaric acid	0.8	i 4.00 h	0.553	12	0.0	
30.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 0.4 ml 0.5*M* KI + 1.5 ml 0.2*M* tartaric acid + 3 ml alc.						no ppt.
31.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.1*M* KI + 3 ml 0.1*M* citric ac.	0.5	i 4.00 h	0.593	13	0.0	
32.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 0.4 ml 0.5*M* KI + 1.5 ml 0.2*M* citric acid + 3 ml alc.						no ppt.
33.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 1 ml 0.1*M* H_3PO_4 + 2 ml 0.1*M* KI	0.4	i 4.00 h	0.577	15	0.0	
34.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 2 ml 0.1*M* H_3PO_4 + 2 ml 0.1*M* KI	0.3	i 4.00 h	0.745	13	0.0	
35.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 2.5 ml 0.2*M* H_3PO_4 + 0.4 ml 0.5*M* KI	0.4	i 2.6 h	0.435	13		
36.	4 ml 0.00125*M* Bi + 2.5 ml 0.2*M* H_3PO_4 + 0.4 ml 0.5*M* KI .	0.3	i 2.64 h	0.668	13		3 Bi:2 Py
37.	4 ml 0.00125*M* Bi + 1 ml *M* HNO_3 + 1 ml 0.2*M* H_3PO_4 + 0.4 ml 0.5*M* KI + 3 ml alc.	1.5	i 4.00 h	0.662	14	0.0	

Explanations: Py = Pyramidon; Bi = Bismuth nitrate; i.i.p. = intermediate intersection point at ml titrant; m.r. = molar ratio of [Bi]:[Py]; i = intersection point; h = horizontal maximum optical density line.

TABLE II

Composition: 4 ml 0.00125M $Bi(NO_3)_3$ + 1 ml M HNO_3 + *a* ml supplements + 2 ml 0.1M KI (or 0.4 ml 0.5M KI) + water ad. 10 ml + *x* ml 0.00125M pyramidon (= titrant). Temp. = 20°. Fisher red filter.

Expt. No.	*Supplements*	*% Bi*	*Found* *Initial ppt. at ml*	*ml titrant at first max. p.*	*Max. optical density value*	*Titration time in min*	*% error*	*Remarks*
38.	1 ml 0.1M $Ca(NO_3)_2$	20.8	0.2	i 4.00 h	0.465	13	0.0	
39.	1 ml 0.1M $Ca(NO_3)_2$ + 3 ml alc.		1.6	i 4.00 h	0.409	13	0.0	
40.	1 ml 0.1M $Ba(NO_3)_2$	7	0.2	i 3.95 h	0.553	14	1.2	
41.	1 ml 0.1M $Mg(NO_3)_2$	30	0.3	i 4.00 h	0.423	13	0.0	
42.	1 ml 0.1M $Mg(NO_3)_2$ + 3 ml alc.		1.5	i 4.00 h	0.638		0.0	i 2.8; i 3.5
43.	1 ml 0.1M $Zn(NO_3)_2$	13.8	0.2	i 4.00 h	0.662	12	0.0	
44.	1 ml 0.1M $Zn(NO_3)_2$ + 3 ml alc.		1.4	i 4.02 h	0.770	13	0.5	
45.	1 ml 0.1M $Mn(NO_3)_2$	16	0.4	i 4.00 h	0.620	12	0.0	
46.	1 ml 0.1M $Mn(NO_3)_2$ + 3 ml alc.		1.6	i 4.00 h	0.561	12	0.0	
47.	1 ml 0.1M $Ni(NO_3)_2$	15.1	0.4	i 3.97 h	0.545	14	0.7	
48.	1 ml 0.1M $Ni(NO_3)_2$ + 3 ml alc.		1.6	i 4.00 h	0.585	14	0.0	
49.	1 ml 0.1M $Co(NO_3)_2$	15	0.5	i 4.00 h	0.557	12	0.0	
50.	1 ml 0.1M $Co(NO_3)_2$ + 3 ml alc.		1.5	i 4.00 h	0.502	12	0.0	i.i.p. 2.7
51.	1 ml 0.1M $Al(NO_3)_3$	28	0.4	i 4.00 h	0.678	13	0.0	
52.	1 ml 0.1M $Al(NO_3)_3$ + 3 ml alc.		1.6	i 4.00 h	0.577	13	0.0	
53.	1 ml 0.1M $Fe(NO_3)_3$ + 2 ml 0.1M H_3PO_4	15.9	0.3	i 4.00 h	0.516	13	0.0	i.i.p. 2.55
54.	1 ml 0.1M $Fe(NO_3)_3$ + 0.6 ml 0.33M H_3PO_4 + 3 ml alc.		2.1	i 4.00 h	0.42	13	0.0	i.i.p. 2.5
55.	1 ml 0.1M $Cr(NO_3)_3$	16.8	0.3	i 4.00 h	0.606	12	0.0	
56.	1 ml 0.1M $Cr(NO_3)_3$ + 3 ml alc.		1.45	i 4.00 h	0.620	12	0.0	
57.	1 ml 0.1M $Cd(NO_3)_2$	8.6	0.3	i 4.00 h	0.699	12	0.0	
58.	1 ml 0.1M $Cd(NO_3)_2$ + 3 ml alc.		1.8	i 4.00 h	0.745	12	0.0	

59.	1 ml 0.1*M* $UO_2(NO_3)_2$	4.2	0.3	i 4.00 h	0.782	12	0.0	
60.	1 ml 0.1*M* $UO_2(NO_3)_2$ + 3 ml alc.		1.8	i 4.00 h	0.763	12	0.0	
61.	1 ml 0.1*M* $CuSO_4$	14.1	0.2	i 4.00 h	0.776	12	0.0	
62.	1 ml 0.1*M* $Cu(NO_3)_2$		0.2	i 4.00 h	0.831	12	0.0	
63.	1 ml 0.05*M* $Hg(NO_3)_2$ (+ 4 ml 0.1*M* KI)	9.6	0.2	i 4.00 h	0.854	12	0.0	
64.	1 ml 0.05*M* $Hg(NO_3)_2$ + 3 ml alc.		1.8	i 4.00 h	0.678	13	0.0	
65.	1 ml 0.1*M* $ZrO(NO_3)_2$	10.2	1.0	i 4.00 h	0.585	28	0.0	
66.	1 ml 0.1*M* $ZrO(NO_3)_2$ + 3 ml alc.		1.8	c.i. 4.00 h	0.336	30	0.0	
67.	1 ml 0.1*M* $Ce(NO_3)_3$	7.0	0.2	i 4.00 h	0.745	11	0.0	
68.	1 ml 0.1*M* $Ce(NO_3)_3$ + 3 ml alc.		1.8	i 3.97 h	0.611	11	0.7	i.i.p. 2.45
69.	1 ml 0.1*M* $Th(NO_3)_4$	4.3	0.1	i 4.00 h	0.727	12	0.0	
70.	1 ml 0.1*M* $Th(NO_3)_4$ + 3 ml alc.		1.8	i 4.01 h	0.688	12	0.2	
71.	1 ml 0.1*M* $NaVO_3$	17.2	0.7	i 4.00 h	0.653	15	0.0	
72.	1 ml 0.1*M* $NaVO_3$ + 3 ml alc.		3.2	i 4.00 h	0.276	15	0.0	
73.	1 ml 0.05*M* Na_2MoO_4	18	0.8	i 4.03 h	0.553	13	0.7	
74.	1 ml 0.05*M* Na_2MoO_4 + 3 ml alc.		2.1	i 4.00 h	0.420	17	0.0	
75.	1 ml 0.05*M* Na_2WO_4	10.8	0.3	i 4.00 h	0.678	18	0.0	
76.	1 ml 0.05*M* Na_2WO_4 + 3 ml alc.		1.9	i 4.00 h	0.468	16	0.9	
77.	1 ml 0.05*M* $SnCl_2$	15.1	1.4	i 3.9 h	0.328	15	2.5	
78.	1 ml 0.05*M* $SnCl_2$ + 3 ml alc.							no ppt.

Explanations: i = intersection point; h = horizontal maximum optical density line; c = contact point; i.i.p = intermediate intersection point at ml titrant; Bi = Bismuth nitrate.

(= pyramidon) giving a final compound of composition 1 : 1. Evidently the phosphoric acid participated in the reaction through partial complex-formation with bismuth and stopped further reaction of bismuth with pyramidon. Whether a neutral salt or a specific anion in a given concentration disturbed the reaction, or even acted detrimentally or not, depended on the amount of bismuth being analyzed. This can be seen by comparing titrations with 4 ml 0.001 *M* Bi (Expts. 8–11) and 5 ml 0.001 *M* Bi (Expts. 20–28). Only in the latter case could titrations be carried out in the presence of nitrate, sulphate, chloride and bromide. *On increasing, even only slightly, the amount of bismuth in the titrated solution, it was possible to counteract the detrimental effect of neutral salts.* Thus, at the higher concentration of bismuth, chloride, present in a molar ratio of 1 Bi:20 Cl, was without influence (Expt. 24), while the bromide at this concentration reduced the maximum density value (Expt. 26). Large excesses of sulphate or nitrate also reduced the sensitivity.

Intermediates. On inspecting the titration curves of Fig. 1, it was interesting to establish that, in addition to the final critical point at 1 Bi:1 Py, more intermediate critical points were also obtained at definite molar ratios of bismuth to pyramidon. It must be emphasized that at all these points the ratios were always *higher* than 1 Bi:1 Py. In this investigation ratios less than 1:1 were never detected. It can, therefore, be concluded that such compounds do not exist. From the intermediate critical points it is evident that compounds of the following molar ratios of metal to pyramidon exist (in this work the ratios are always designated with the bismuth first).

$$4{:}1\uparrow\downarrow \xrightarrow{+\text{ Py}} 3{:}1\downarrow \xrightarrow{+\text{ Py}} 2{:}1\downarrow \xrightarrow{+\text{ Py}} 3{:}2\downarrow \xrightarrow{+\text{ Py}} 1{:}1\downarrow\downarrow$$

Probably the appearance of each of these points depended on the differences in solubility of the compounds concerned under the specific working conditions. Even intermediate compounds which were clear and certain depended on whether some alcohol was present or not. In the alcohol some of the intermediates were more soluble and therefore disappeared (compare Expts. 13 and 16). Thus the intermediate 4:1 was soluble in alcohol and ammonium nitrate. The compound 2:1 appeared in ordinary cases and in the absence of supplements (Expts. 13, 20 and 22). The existence of the above intermediates was also confirmed in the reverse titrations using bismuth nitrate as titrant (see below).

Foreign metals

There are probably no foreign metals which should be absent in the titrated solution, but in contrast to previous investigations their permitted concentrations were far lower. Generally the foreign cations could make up 80–90% of the total metal content in this investigation. In exceptional cases the percentage was even higher (see thorium). Probably it was not the foreign *metal* but the foreign *salt* which disturbed. The upper limits were not determined in each case, so that the percentage of bismuth may be much lower than that which is given in the table in special cases. Table II gives a compilation of such titrations. From the table it can be seen that *all titrations without exception were successful when the percentage of the foreign metal was* less *than* 50%. The error was always close to zero. In the presence of ferric iron the addition of phosphoric acid masked the iron entirely (Expts. 53 and 54). (In both experiments the intermediate 3 Bi:2 Py was also traced.) In all cases parallel titrations with some alcohol present were also carried out. These titrations are of special interest because they give the end-point of the final compound 1:1 directly as the solubility of the intermediates of compositions 4:1, 3:1 or 3:2 is increased in alcohol. However, in some cases the maximum optical density value was also reduced.

Bismuth nitrate as titrant

Working with similar compositions as in the basic experiments of Table I, reverse titrations were carried out using bismuth nitrate as titrant. These experiments are of special interest as similar titrations may be carried out in the presence of other complicated heterocyclic nitrogen compounds, alkaloids, etc. The results of such a study will be presented in a special report. The titrations of pyramidon with bismuth were very instructive because they provided a deep insight into the compositions of the intermediates which appeared in the system before the final compound was obtained. A compilation of selected experiments is presented in Table III and in Fig. 2. All titrations proceeded as smoothly as before. The titrations lasted 10–15 min and the end-point was always clear-cut with negligible errors. The numerical values of the intermediate critical points, as far as they could be safely taken from the titration curves, are also given in the table. The maximum optical density values obtained were proportional to the amount of pyramidon in solution. These titrations can therefore be used with the same success for the determination of the organic compound.

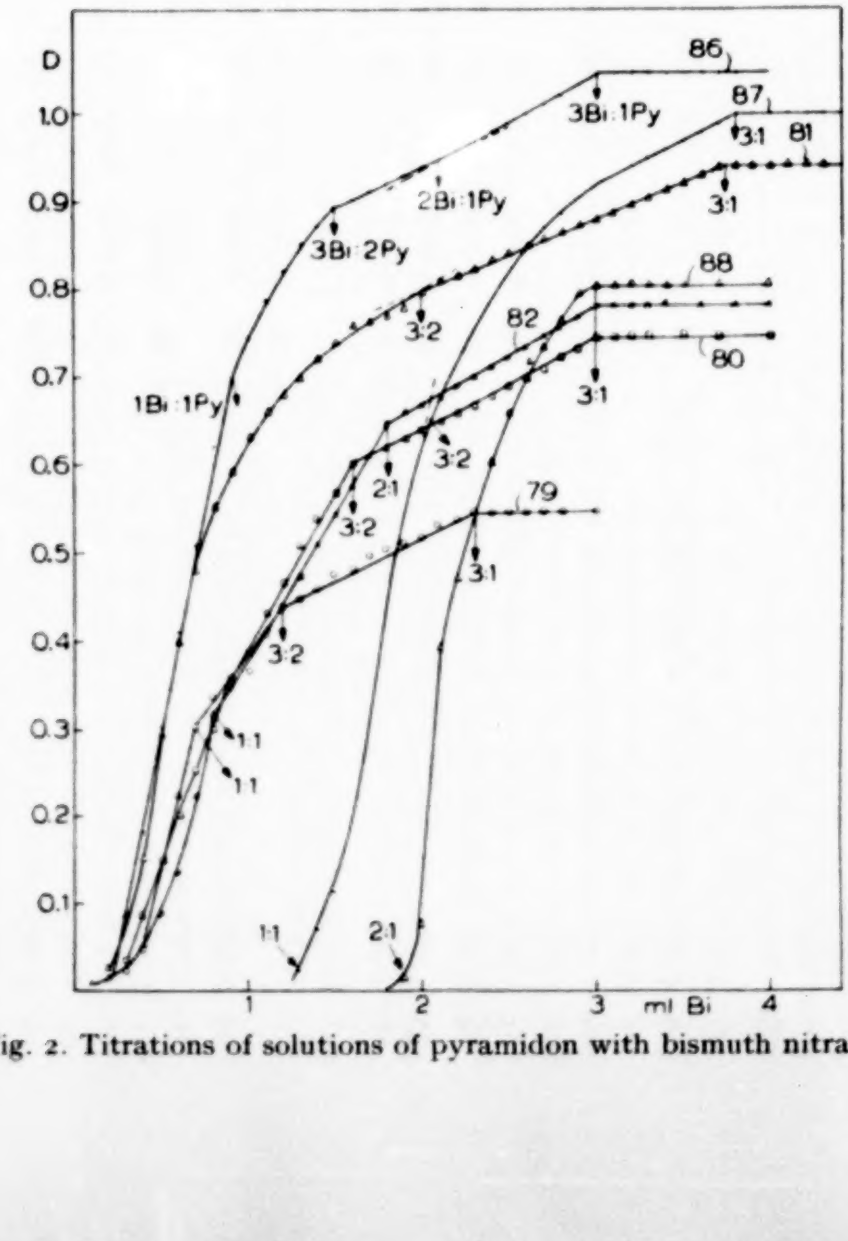

Fig. 2. Titrations of solutions of pyramidon with bismuth nitrate.

TABLE III

Composition: *a* ml *kM* Pyramidon (= Py) + 1 ml *M* HNO_3 + *b* ml *lM* KI [or *b* ml *mM* $Bi(NO_3)_3$ (= Bi)] + *c* ml alcohol + (9—*a*—*b*—*c*) ml H_2O + *x* ml *nM* titrant. Temp. = 20°. Filter: red. Titration time: 10–15 min.

Expt. No.	*Titrated solution contained*	*Titrant*		*Initial ppt. at ml titrant*	*Found*										
					Molar ratios of	*1st critical point*			*2nd critical point*			*Final crit. point*			*Error in final point*
		Name	*Molarity*			*At ml*	*Opt. density*	*Molar ratio*	*At ml*	*Opt. density*	*Molar ratio*	*At ml*	*Opt. density*	*Molar ratio*	
79.	3 ml 0.00125*M* Py + 2 ml 0.1*M* KI	Bi	0.005	0.2	Bi : Py	0.7	0.30	1:1	1.2	0.44	3:2	i 2.23 h	0.54	3:1	0.9
80.	4 ml 0.00125*M* Py + 2 ml 0.1*M* KI	Bi	0.005	0.1	Bi : Py							i 3.0 h	0.75	3:1	0.0
81.	5 ml 0.00125*M* Py + 2 ml 0.1*M* KI	Bi	0.005	0.2	Bi : Py				c 2.0	0.80	3:2	i 3.75 h	0.94	3:1	0.0
82.	4 ml 0.00125*M* Py + 4 ml 0.1*M* KI	Bi	0.005	0.2	Bi : Py				i 1.8	0.64	2:1	i 3.00 h	0.78	3:1	0.0
83.	5 ml 0.00125*M* Py + 1.2 ml 0.5*M* KI	Bi	0.005	0.1	Bi : Py				1.9	0.79	3:2	i 3.70 h	0.93	3:1	1.0
84.	6 ml 0.00125*M* Py + 0.8 ml 0.5*M* KI	Bi	0.005	0.1	Bi : Py				i 1.50	0.77	1:1	i 4.50 h	1.17	3:1	0.0
85.	4 ml 0.00125*M* Py + 2 ml 0.05*M* KI	Bi	0.005	0.2	Bi : Py	0.9	0.70	1:1	i 1.7	0.67	3:2	i 3.00 h	0.85	3:1	0.0
86.	4 ml 0.00125*M* Py + 2 ml 0.1*M* KI + 3 ml alc.	Bi	0.005	0	Bi : Py				c 1.50	0.89	3:2	i 3.00 h	1.05	3:1	0.0
87.	1.25 ml 0.005*M* Py + 2 ml 0.1*M* KI + 5 ml alc.	Bi	0.005	$\sim$1.3	Bi : Py	$\sim$1.3	i.ppt.p.	1:1	1.95	0.63	3:2	i 3.80 h	1.00	3:1	$\sim$1.0
88.	2 ml 0.0025*M* Py + 2 ml 0.1*M* KI + 5 ml alc.	Bi	0.005	$\sim$1.9	Bi : Py	$\sim$1.9	i.ppt.p.	2:1				i 2.95 h	0.80	3:1	$\sim$1.5
89.	2 ml 0.0025*M* Py + 1.6 ml 0.5*M* KI + 5 ml alc.	Bi	0.005									$>$5.0	0.0		
90.	2–4 ml 0.1*M* KI	Bi	0.005	$>$5.0								$>$5.0	0.0		
91.	4 ml 0.00125*M* Bi	KI	0.025	$>$5.0								$>$5.0	0.0		
92.	6 ml 0.0025*M* Bi	KI	0.04	$>$5.0								$>$5.0	0.0		
93.	4 ml 0.00125*M* Py + 4 ml 0.00125*M* Bi	KI	0.0166		Bi : I^-	1.2	i.ppt.p.	1:4				i 2.40 h	0.42	1:8	0.0
94.	2 ml 0.0016*M* Py + 4 ml 0.0025*M* Bi	KI	0.025	0.75	Bi : I^-	0.75	i.ppt.p.	1:2	c 1.6	0.72	1:4	i 3.20 h	0.83	1:8	0.0

95. 4 ml 0.00166*M* Py + 4 ml 0.0025*M* Bi	KI	0.025		Bi : I^-	0.55	i.ppt.p.	1:2				i 3.20 h	0.85	1:8	0.0
96. 3 ml 0.0033*M* Py + 4 ml 0.0025*M* Bi	KI	0.025		Bi : I^-	0.6	i.ppt.p.	1:2				i 3.20 h	0.72	1:8	0.0
97. 1 ml 0.01*M* Py + 4 ml 0.00125*M* Bi	KI	0.0166	0.6	Bi : I^-	0.6	i.ppt.p.	1:2				i 2.40 h	0.83	1:8	0.0
98. 2 ml 0.01*M* Py + 4 ml 0.00125*M* Bi	KI	0.0125	0.8	Bi : I^-	0.8	i.ppt.p.	1:2				i 3.20 h	0.88	1:8	0.0
99. 4 ml 0.01*M* Py + 4 ml 0.00125*M* Bi (+ 1.3 ml *M* HNO_3)	KI	0.0125	~0.8	Bi : I^-	~0.8	i.ppt.p.	1:2	~1.5	0.59	1:4	i 3.20 h	0.85	1:8	0.0
100. 3 ml 0.02*M* Py + 4 ml 0.00125*M* Bi (+ 1.5 ml *M* HNO_3)	KI	0.0125	~0.8	Bi : I^-	~0.8	i.ppt.p.	1:2	i≥1.5	0.55	1:4	i 3.20 h	0.82	1:8	0.0
101. 4 ml 0.02*M* Py + 4 ml 0.00125*M* Bi (+ 1.5 ml *M* HNO_3)	KI	0.0125	0	Bi : I^-	0.75	i.ppt.p.	1:2				c 1.6 h	0.69	1:4	~0.0
102. 6 ml 0.02*M* Py + 2 ml 0.0025*M* Bi (+ 1.6 ml *M* HNO_3)	KI	0.0125	~0.7	Bi : I^-	~0.7	i.ppt.p.	1:2				i 1.55 h	0.68	1:4	
103. 4 ml 0.02*M* Py + 2 ml 0.0025*M* Bi (+ 0.5 ml 3*M* HNO_3) + 3 ml alc.	KI	0.0125		Bi : I^-	0.75	i.ppt.p.	1:2				c 1.6 h	0.68	1:4	~0.0
104. 4 ml 0.02*M* Py alc. + 4 ml 0.00125*M* Bi aq. (+ 0.5 ml 3*M* HNO_3) + 1 ml alc.	KI	0.0125	≥1.5	Bi : I^-							i 1.6 h	0.50	1:4	
105. 4 ml 0.02*M* Py aq. + 4 ml 0.00125*M* Bi aq. (+ 1.5 ml *M* HNO_3)	KI	0.0063	~1.7	Bi : I^-	~1.7	i.ppt.p.	1:2				i 3.26 h	0.53	1:4	
106. 4 ml 0.02*M* Py aq. + 2 ml 0.0025*M* Bi (+ 0.5 ml 3*M* HNO_3) + 3 ml alc.	KI	0.0063	~1.7	Bi : I^-	~1.7	i.ppt.p.	1:2				i 3.20 h	0.63	1:4	
107. 4 ml 0.02*M* Py alc. + 4 ml 0.00125*M* Bi aq. (+ 0.5 ml 3*M* HNO_3) + 1 ml alc.	KI	0.0063	~2.6	Bi : I^-	~2.6						i 3.20 h	0.41	1:4	~0.0

Explanations: c = contact point; i = intersection point; h = horizontal maximum optical density line; i.ppt.p. = initial precipitation point; Bi = Bismuth nitrate; Py = Pyramidon.

Composition. It was interesting to establish that in these experiments the composition of the final compound $(=\downarrow\downarrow)$ was always 3 Bi:1 Py. The critical point at the ratio of 1:1 was hardly observed at all in these experiments. The compounds which were normally deduced from the curves showed the following ratios of bismuth to pyramidon:

$$1:1\downarrow \xrightarrow{+\,\mathrm{Bi}} 3:2\downarrow \xrightarrow{+\,\mathrm{Bi}} (2:1)\downarrow \xrightarrow{+\,\mathrm{Bi}} 3:1\downarrow\downarrow$$

The compound 2:1 appeared either in alcoholic solution or when more potassium iodide than usual was present (Expts. 82 and 88). The compound 3:2 was the most usual and clear intermediate.

Potassium iodide as titrant

At the beginning of this investigation an effort was made to find the optimum amount of potassium iodide necessary for the safe titration of bismuth. It was found that this amount was not critical as far as upper limits were concerned, as excesses of iodide were without influence. Therefore, most of our previous titrations were carried out with a constant amount of iodide. Here, our interest was to ascertain the minimum amount of iodide necessary for the reaction concerned, and to study the reaction with iodide in general. A selection of such titrations, their compositions and results are compiled in Table III and Fig. 3. Titrations with as high a concentration as 0.1 *M* KI were carried out; the results of these experiments showed that in all cases after the formation of the final insoluble compound, a maximum horizontal density line was obtained and the end-point remained unchanged even upon the addition of a tenfold excess of iodide. The amount of bismuth which was present in the solutions was practically constant, while the molar ratio of [Bi]:[Py] was varied from 2:1 to 1:16.

The precision of the end-points of course depended on the concentration of potassium iodide used. Under our working conditions a minimum of 3 ml of titrant was necessary in order to obtain a precise end-point. Such titrations always gave end-points at the theoretically calculated ratio of either 1 Bi:4 I^- or 1 Bi:8 I^-. Therefore, *potassium iodide could be used with the same success as pyramidon for the titration of bismuth.* The sensitivity and the precision were of the same order with both titrants. It was interesting to establish that even when the molar amount of pyramidon was as low as $^1/_3$ of the molar amount of bismuth the end-point obtained was still normal (Expts. 94 and 95). The end-point occurred here, as in many other cases, exactly at the molar ratio of 1 Bi:8 I^-.

Composition. On varying the amount of pyramidon in the solutions between the limits of the ratio of [Bi]:[Py] from 3:1 to 1:12, the same end-point was always obtained at the ratio 1 Bi:8 $I^-\downarrow\downarrow$. However, when the amount of pyramidon present was greater than the ratio of 1 Bi:12 Py, the final point of the titration occurred at the ratio 1 Bi:4 I^- (see Expts. 99, 102). The intermediate compounds obtained were at the following ratios of bismuth to iodide:

$$1:2\uparrow \xrightarrow{+\,I^-} 1:4\downarrow\downarrow$$

or:

$$1:2\uparrow \xrightarrow{+\,I^-} (1:4\downarrow) \xrightarrow{+\,I^-} 1:8\downarrow\downarrow$$

Sensitivity. With the same amount of bismuth, the maximum density values, and therefore the sensitivity of the reaction, were exceedingly high (at the ratio of 1 Bi:8 I^-) when the molar amount of pyramidon in the titrated solutions was from twice to twelve times (critical concentration!) that of the bismuth. Within these concentrations the density was independent of the amount of pyramidon in solution. *It may, therefore, be concluded that these are the optimum conditions for a sensitive and precise titration of bismuth with potassium iodide.*

DISCUSSION

The impression gained from the results obtained is that the presentation of the insoluble compound concerned as $RN \cdot BiI_4$ only partly reflects the real structure and composition of the insoluble compounds studied by us. In gravimetric work the conditions are always uniform and therefore the above compound was always obtained. In contrast, in heterometry the working conditions were changed, as each of the three reacting components was used as titrant and studied separately. Altogether a series of intermediate compounds was obtained in addition to the *four* different *final* com-

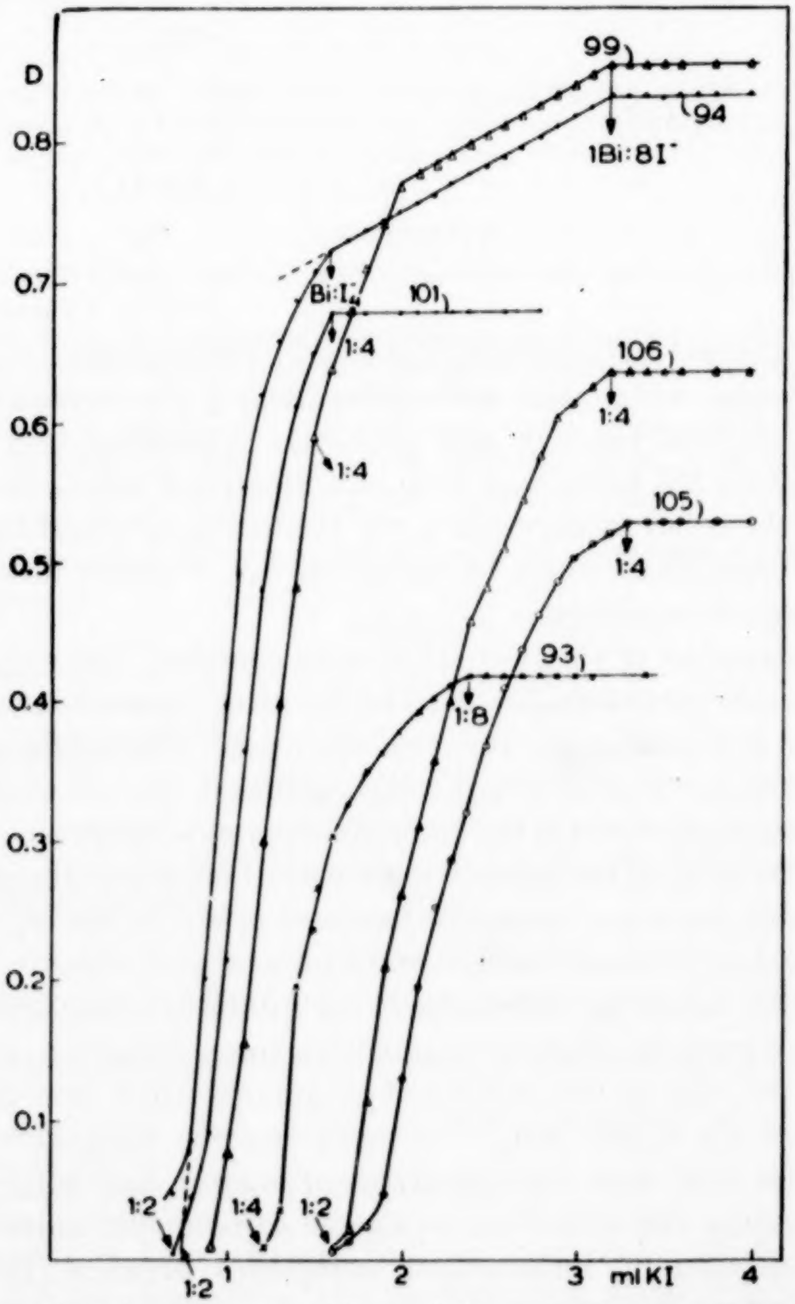

Fig. 3. Titrations of mixtures of pyramidon and bismuth nitrate with potassium iodide.

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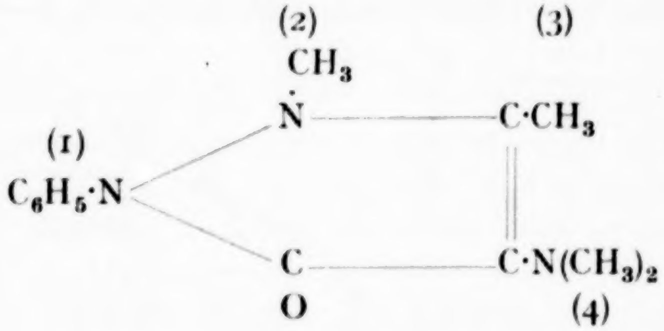
pounds which were studied. It was interesting to establish that the composition of all the final compounds was strictly constant and that each of them could be used with almost equal success for a precise determination of either bismuth or pyramidon. Amongst the intermediates traced a compound with the composition $Bi_3Py_2I_n$ was found. This compound must consist of at least two nuclei, each of which has the composition $PyBiI_m$, joined by a bismuth bridge. Therefore it may be deduced with certainty that the final compounds obtained are of quite complex structure. The same is the case with the anion $[BiI_8]^{-5}$ which was so often encountered by us. It is remarkable that the stoichiometry of the compounds is strictly maintained. On analyzing the conditions for the formation of the compounds having the compositions $PyBiI_n\downarrow\downarrow$ and $PyBi_3I_m\downarrow\downarrow$ it is seen (from the intermediates) that the latter was formed by the gradual addition of bismuth or better $[BiI_n]^{-(n-3)}$ to the former compound. Pyramidon which has the following structure



has three nitrogen atoms and it may well be that all three are saturated by the addition of $HBiI_n$. Conversely, on titrating with pyramidon, at the beginning of the titration there is a large excess of bismuth and only little pyramidon, and consequently the correct conditions for the formation of an intermediate $PyBi_3I_m$ exist. This intermediate as well as the other intermediates are finally transformed into the compound $PyBiI_n\downarrow\downarrow$. Therefore the results of titrations are compatible with the nitrogen content of the organic compound.

As to the composition of the bismuth–iodide complex, this may change with the organic base used. It is remarkable that, on titrating bismuth–pyramidon mixtures with a potassium iodide solution, the *final* compound only contained $[BiI_8]^{-5}$ anions even where the molar ratio was 1 Py to 3 Bi in solution. The anion complex $[BiI_8]^{-5}$ in which the coordination number of Bi^{+3} is 8 was often encountered in our work. Actually a high coordination number for bismuth is known although not satisfactorily explained. This high charge of the anion cannot be balanced solely by the organic base. It may, therefore, well be that H^+ ions coming from the mineral acid, which is present in the solution, participate in balancing the charge in the insoluble compound found. The question of whether an insoluble final compound with anion $[BiI_4]^-$ or $[BiI_8]^{-5}$ was formed depended (see Table III) on the excesses of pyramidon which were present in solution. If we accept that the anion $[BiI_8]^{-5}$ actually has the composition $[H_nBiI_8]^{-(5-n)}$, then it is plausible that high concentrations of organic base neutralize the H^+ ions and therefore destroy the above ion giving the more simple anion $[BiI_4]^-$. Another interesting fact is that no intermediate complexes between $[BiI_4]^-$ and $[BiI_8]^{-5}$ were found.

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Analytical aspect

General

A red filter must be used. In each case the end-point of the titration coincides with the first maximum optical density point, after which a horizontal density line is obtained. The titration time is 10–15 minutes and the error is always close to zero.

Bismuth

Titration with pyramidon. Approximately *one* mg bismuth as nitrate in 10 ml solution can be determined by titration with a $\sim 0.00125M$ aqueous solution of pyramidon. The titrated solution must contain: 1 ml M nitric acid and 2 ml $0.1M$ potassium iodide. The analyzed solution may contain the following metals as cations or anions, which make up 80–90% of the total metal content: Ca^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}, Al^{+3}, Fe^{+3}, Cr^{+3}, Cd^{+2}, $(UO_2)^{+2}$, Cu^{+2}, Hg^{+2}, $(ZrO)^{+2}$, Ce^{+3}, Th^{+4}, Sn^{+2}, VO_3^-, MoO_4^{-2} and WO_4^{-2}. The end-point lies exactly at the molar ratio of 1 Bi : 1 Py.

Titration with potassium iodide. Approximately *one* mg bismuth as nitrate in 10 ml solution can be determined by titrating with a $\sim 0.0125M$ aqueous solution of potassium iodide. The solution must contain 1–1.5 ml M nitric acid and 1–4 ml $0.01M$ pyramidon. The end-point lies exactly at the molar ratio of 1 Bi : 8 I^-.

Remark. If the amount of pyramidon is equal to 6 ml $0.01M$ pyramidon or more, the end-point lies exactly at the molar ratio of 1 Bi : 4 I^-. The first method is preferable.

Pyramidon

Titration with bismuth nitrate. Approximately 1.2 mg pyramidon in 10 ml solution which contains 1 ml M nitric acid and 2 ml $0.1M$ potassium iodide are titrated with a $\sim 0.005M$ aqueous bismuth nitrate solution. The end-point lies exactly at the molar ratio of 3 Bi : 1 Py.

SUMMARY

The reaction between iodide, bismuth and pyramidon and the composition of the compounds obtained were thoroughly studied.

At least four final insoluble compounds were obtained; each of them could be used with the same success for a precise determination of either bismuth or pyramidon. The molar ratios of bismuth to pyramidon found were 1 : 1 or 3 : 1; the ratios of bismuth to iodide were 1 : 4 or 1 : 8.

Analytical methods are presented for the determination of approximately *one* mg bismuth (or pyramidon) in the presence of 80–90% of the following cations or anions: Ca^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}, Al^{+3}, Fe^{+3}, Cr^{+3}, Cd^{+2}, $(UO_2)^{+2}$, Cu^{+2}, Hg^{+2}, $(ZrO)^{+2}$, Ce^{+3}, Th^{+4}, Sn^{+2}, VO_3^-, MoO_4^{-2} and WO_4^{-2}.

The titrations always lasted 10–15 min and the error was practically negligible.

RÉSUMÉ

Les auteurs ont étudié la réaction entre un iodure, le bismuth et le pyramidon, ainsi que la constitution des composés obtenus. Par cette réaction, il est possible de doser avec précision soit le bismuth, soit le pyramidon.

ZUSAMMENFASSUNG

Es wird die Reaktion zwischen Jodid, Wismut und Pyramidon sowie die Zusammensetzung der Reaktionsprodukte untersucht. Mit Hilfe dieser Reaktion kann sowohl Wismut wie auch Pyramidon sehr genau bestimmt werden.

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THE DETERMINATION OF NITROGEN IN NITROCELLULOSE

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INTRODUCTION

The usual method of determining the nitrogen content of nitrocellulose involves the use of the nitrometer[1]. In this method the volume of nitric oxide liberated when a solution of nitrocellulose in sulphuric acid is shaken with mercury is correlated to the nitrogen content of the sample. Although capable of giving good results in the hands of an experienced operator, this method requires much practice and can be dangerous in the event of a nitrometer breaking during shaking.

In an effort to find an easier but equally accurate method, that of SHAEFER AND BECKER[2] was studied. This gave erratic results, however, and the source of error was not discovered. A procedure given by STALCUP AND WILLIAMS[3] was found to be more satisfactory, and after modification of the method, very precise results for both nitrocellulose and potassium nitrate were obtained. Moreover, the method was considerably more convenient for routine use than the nitrometer procedure.

EXPERIMENTAL

Briefly, STALCUP AND WILLIAMS' procedure[3] is as follows: The sample (about 0.3 g) is stirred with 10 ml of 98% sulphuric acid until dissolved. Within 20 min of the sulphuric acid addition, 10 ml of salicylic acid solution is added and the mixture allowed to stand for 10 min. Reduction is effected by refluxing for 1 min with 75 ml of 0.3N titanous chloride solution in an atmosphere of nitrogen. The solution is cooled and, while the inert atmosphere is maintained, the excess titanous ion is titrated with ferric ammonium sulphate using ammonium thiocyanate as indicator. A blank determination is run concurrently.

Using this procedure, the results obtained for a nitrocellulose sample containing 12.91% nitrogen (nitrometer) were unsatisfactory. Nine determinations gave a mean value of 12.99% nitrogen and a standard deviation of 0.11. In an attempt to locate the source of error, a homogeneous batch of nitrated salicylic acid was prepared and its nitrogen determined by reduction with titanous chloride. It was found that the time and temperature of the reduction were critical. When the STALCUP AND WILLIAMS' procedure was modified so that reduction was effected at room temperature for 30 min, the mean of 4 determinations was 9.68% nitrogen with a standard deviation of 0.021. Comparable figures for 12 determinations following the STALCUP AND WILLIAMS' method were 9.63 and 0.063.

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A fairly large excess of titanous chloride was required to obtain results agreeing with those of nitrometer determinations as shown in Table I.

TABLE I

EFFECT OF VOLUME OF TITANOUS CHLORIDE

Approximate excess of 0.4 N $TiCl_3$ (ml)	*No. of determination*	*Mean nitrogen content obtained (%*	*Standard deviation*
5	5	12.40	0.040
15	5	12.95	0.020
25	5	12.95	0.020

The nitrogen content according to nitrometer determinations was 12.94%.

As a result of this experiment the volume of titanous chloride (not less than 0.38*N*) was set at 50 ml and the weight of sample was reduced from 0.3 g to 0.20–0.22 g.

Factorial experiment

The errors in the method were finally assessed in a factorial experiment[4]. The factors investigated and their levels are summarized in Table II.

TABLE II

FACTORIAL EXPERIMENT

	Factor	*Levels*	
A	Amount of sulphuric acid added to sample	8 ml	12 ml
B	Time of contact between sample and sulphuric acid	5 min	10 min
C	Amount of salicylic acid solution added	8 ml	12 ml
D	Time of standing with salicylic acid solution	10 min	20 min
E	Reduction time with titanous chloride	15 min	30 min

The levels for factors A, C and D correspond approximately to STALCUP AND WILLIAMS' conditions and were chosen to determine how closely these conditions must be adhered to. The levels of factor E were based on the considerations mentioned above, while those for B were governed by the fact that low results were obtained in preliminary experiments if the nitrocellulose was allowed to remain in contact with sulphuric acid for as long as 20 min as indicated by STALCUP AND WILLIAMS.

The experiment, with a nitrocellulose sample of 12.90% nitrogen (nitrometer), showed that only factors B and E affected the result. The mean per cent nitrogen found was 12.853 and the significant factors had the following effects:

B. Increase in time of contact from 5–10 min resulted in a mean decrease of 0.073% nitrogen.

E. Increase in reduction time from 15–30 min resulted in a mean increase of 0.054% nitrogen.

A later experiment showed that it was necessary to increase the reduction time to 45 min in order to obtain accurate results.

In the method finally chosen, therefore, the levels of the non-significant factors (A, C and D) were set at the mean of the values shown in Table II, and the contact and reduction times were 5 and 45 min respectively. Under these conditions the mean result of 16 determinations, carried out on recrystallized reagent-grade potassium nitrate was 13.844% nitrogen, with a standard deviation of 0.012 (the theoretical value is 13.85% nitrogen). It was found to be necessary to dry the potassium nitrate for 2–3 h at 240° in order to remove last traces of water from the crystals.

To determine the suitability of the method for routine work, analyses were carried out by a different operator. A similar batch of potassium nitrate was used and ten determinations resulted in a mean of 13.830% nitrogen with a standard deviation of 0.014, showing that there is no significant operator bias.

Comparison with the nitrometer

To illustrate the reasonable agreement between the transnitration and the nitrometer methods, results using both methods are given in Table III.

TABLE III

COMPARISON OF NITROGEN CONTENTS OF NITROCELLULOSE SAMPLES OBTAINED BY THE NITROMETER AND TRANSNITRATION METHODS

Sample	*Nitrometer A (Operator A)*	*Nitrometer B (Operator B)*		*Transnitration (Operator C)*	
1	11.84	11.93	11.94	11.88	11.90
2	11.91	11.91	12.01	11.92	11.93
3	11.95			11.99	11.99
4	12.11			12.05	12.07

Precision of the method under routine conditions

Routine determinations of the nitrogen content of nitrocotton and guncotton were carried out in duplicate and the standard deviation was calculated from the differences between duplicates. The standard deviation of the results of an experienced operator was 0.012 (6 degrees of freedom) while for an operator who was new to the method the standard deviation was 0.023 (5 degrees of freedom). For comparison, the standard deviations of the results of two operators experienced in the nitrometer method were 0.025 (17 degrees of freedom) and 0.019 (10 degrees of freedom).

RECOMMENDED PROCEDURE

Reagents

Ferric ammonium sulphate (0.4*N*). 195 g analytical reagent-grade ferric ammonium sulphate and 25 ml 98% sulphuric acid per litre. Filter and standardise the solution by gravimetric determination of the iron content. Alternatively, standardise the solution by carrying out the determination with a material of known nitrogen content. A suitable material is analytical reagent-grade potassium nitrate which has been dried for 2–3 h at 240°.

Titanous chloride solution (0.4*N*). Mix 2500 g of B.D.H. titanous chloride solution (approximately 12.5%) and 250 ml of concentrated hydrochloric acid. Filter under a blanket of nitrogen, and make up to about 4 l in an aspirator which has been painted to protect the solution from light. Dispense the solution by means of a 50-ml burette, the aspirator, burette and a Kipp carbon dioxide apparatus being inter-connected so as to exclude all air. Adjust the strength of the solution to 0.39–0.41*N*, and standardise regularly by titration with ferric ammonium sulphate solution.

Ammonium thiocyanate solution. 200 g/l.

Salicylic acid solution. Dissolve 100 g of salicylic acid in a mixture of 900 ml 98% sulphuric acid and 100 ml glacial acetic acid. Although slight precipitation sometimes occurred on prolonged standing, the solution was still suitable for use.

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(It is stressed that the procedure given below must be rigidly adhered to in order to obtain precise results.)

Weigh accurately 0.2–0.22 g of sample into a dry 50-ml beaker. Add 10 ml of concentrated sulphuric acid and stir and crush the sample with a glass rod to aid solution. Exactly 5 min after the addition of the sulphuric acid, and even if the sample is not completely dissolved, add 8 ml of salicylic acid solution. Stir until solution is complete. Allow the solution to stand for 10–15 min and transfer into a 500-ml refluxing (reduction) flask fitted with gas inlet. Wash the solution remaining in the beaker into the reduction flask, using about 15-ml portions of distilled water. The total volume of water should be 45–50 ml. The water must be added very slowly otherwise darkening will occur. Cool the flask in running water and swirl carefully to mix the solution. Connect the gas inlet of the flask to a supply of nitrogen (*via* a wash bottle containing about 20 ml of water to act as a flow meter) and displace the air from the flask with nitrogen. Add exactly 50 ml of titanous chloride swirling occasionally during the addition. Allow the solution to stand for 45–50 min under a continuous flow of nitrogen. The nitrogen flow should produce a faint ripple on the surface. Add 1–2 ml of ammonium thiocyanate solution and titrate the excess titanous ion with ferric ammonium sulphate. Maintain the nitrogen flow continuously during the titration. Titrate slowly near the end-point. Wash down the walls of the flask and the tip of the burette with water and continue titrating until the first appearance of a permanent orange-red colour. Carry out a reagent blank under the same conditions as above. The nitrogen content of the sample is given by[3]:

$$\%\text{N} = \frac{\text{ml of TiCl}_3\text{ oxidised} \times \text{normality of TiCl}_3 \times 0.2335}{\text{weight of sample}}$$

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SUMMARY

A method for the determination of nitrogen in nitrocellulose has been developed. The sample is dissolved in concentrated sulphuric acid and a salicylic acid solution is added. The nitrosalicylic acid formed is reduced at room temperature with an excess of titanous chloride solution and the excess is estimated by titration with ferric alum. Statistically designed experiments were used to establish the conditions necessary for accurate results. The procedure is more rapid than the usual nitrometer method and gives results of high precision; *e.g.* on a mean result of about 13.8% nitrogen, the standard deviation is 0.014.

RÉSUMÉ

Une méthode est proposée pour le dosage de l'azote dans la nitrocellulose. L'échantillon à analyser est dissous dans l'acide sulfurique concentré. On ajoute une solution d'acide salicylique. L'acide nitrosalicylique formé est réduit par un excès de chlorure titaneux; cet excès est ensuite déterminé par titrage au moyen d'alun ferrique.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung des Stickstoffs in Nitrocellulose beschrieben. Die Nitrocellulose wird in conc. Schwefelsäure gelöst und eine Lösung von Salicylsäure zugegeben. Die hierbei entstandene Nitrosalicylsäure wird mit einem Überschuss von Titan(III)chlorid reduziert und dieser Überschuss durch Titration mit einer Eisenalaunlösung bestimmt.

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SUR LA STABILITÉ THERMIQUE DES ÉTALONS ANALYTIQUES. VI*

CLÉMENT DUVAL

avec la collaboration technique de

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Poursuivant l'étude thermogravimétrique et spectrophotométrique des substances utilisables comme étalons en analyse volumétrique, nous présentons aujourd'hui nos résultats avec 12 nouvelles substances, à savoir: l'acide nitrilotriacétique, le thiosulfate de strontium, le nitrite de sodium, l'acide phosphomolybdique, le paraperiodate de sodium, le persulfate de potassium, le chlorure d'aluminium, le pyrosulfate de sodium, l'alun d'aluminium et d'ammonium, le sulfate de fer(II), le sel de Mohr, l'alun de fer ammoniacal.

Les courbes de thermolyse ont été réalisées comme d'habitude par voie photographique et par voie graphique, sur 200 mg environ de substance et avec une vitesse de chauffe de 300° par heure. Les spectres d'absorption infrarouge ont été enregistrés par la méthode des poudres (au besoin en les agglomérant avec un peu de vaseline) sur un spectromètre Perkin-Elmer 12C, équipé avec un prisme de sel gemme.

Acide nitrilotriacétique

L'acide nitrilotriacétique est parfaitement sec et se montre stable jusqu'à 286° (Fig. 1). La décomposition se produit subitement et le creuset est vidé complètement à 638°.

Le spectre infrarouge, à côté de la bande très forte du carboxyle à 1742 cm^{-1}, indique 722 (aF), 730 (aF), 745 (aF), 865 (F), 902 (TF), 966 (TF), 1010 (TF), 1074 (aF), 1206 (aF), 1238 (aF), 1335 (F) cm^{-1}.

Thiosulfate de strontium

Le produit qui nous a servi comme point de départ, cristallisé au-dessus de 50°, retient 1 molécule d'eau qui disparait très lentement entre 70 et 180° (Fig. 2), plus rapidement ensuite; il faut compter que le départ complet de l'eau n'est pas effectué avant 240° mais alors le sel se dissocie; du soufre se dégage et le palier sensiblement horizontal obtenu entre 350 et 507°, correspond à un mélange de sulfate, de sulfite et de sulfure en évolution. Au-dessus de cette dernière température, le gain d'oxygène devient important et l'on arrive au sulfate de strontium sans sulfure dès 700°. En conclusion, pour faire une liqueur titrée avec cet étalon, on ne dépassera pas 170° pour le séchage du sel.

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* Pour le cinquième mémoire de cette série, voir *Anal. Chim. Acta*, 16 (1957) 545.

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Le spectre infrarouge de ce sel avait déjà été examiné par DUVAL ET LECOMTE[1]. Dans la région de 6 à 15 μ, nous relevons les bandes très fortes: 1019, 1113 et 1166 cm^{-1}.

Nitrite de sodium

Le nitrite de sodium sec, blanc, non hygroscopique, extrait d'un flacon neuf, se montre rigoureusement stable jusqu'à 538°. Commence alors une décomposition lente se prolongeant jusque vers 750°, puis plus rapide entre 792 et 956° et vers 1000°, il reste l'oxyde Na_2O. Nous ne sommes donc pas d'accord avec OSWALD[2] qui indique 320° pour le début de la dissociation, ni avec RÂY[3] qui indique vers 500° une transformation en nitrate; le gain de poids correspondant n'est pas accusé sur notre courbe (Fig. 3).

Dans la région du sel gemme, ce sel donne une bande forte déjà connue pour 825 cm^{-1}; MILLER ET WILKINS[4] donnent 831 (m). Dans l'eau, nous trouvons la bande très forte 1240 et faible 1338 cm^{-1}.

Acide phosphomolybdique

L'acide phosphomolybdique (produit Merck) ne possède pas, comme l'on sait, un degré d'hydratation fixe quoique FINKENER[5] indique la composition $P_2O_5 \cdot 24MoO_3 \cdot 3H_2O + 58H_2O$. Le produit de départ contenait environ $36H_2O$. De son côté DUPUIS[6] a préparé un acide phosphomolybdique contenant 32 molécules d'eau. Parfois le produit de départ en contient un nombre supérieur à 58 molécules et sans aucun accident dans la courbe de thermolyse pour cette teneur en eau. Il en résulte que l'on ne peut pas peser cet acide tel qu'il sort du flacon. Toutefois, lorsqu'on le chauffe à 116°, on arrive à la composition $P_2O_5 \cdot 24MoO_3 \cdot 3H_2O$ qui se maintient jusqu'à 412°. Là commence la déshydratation et de 477 à 757° s'étend le palier du corps anhydre pour notre vitesse de chauffe. Alors commence la sublimation de l'anhydride molybdique qui s'effectue rapidement au-delà de 802°. On possède donc deux formes de pesée: produit à $3H_2O$ et produit anhydre, pour ce corps (Fig. 4).

Le spectre infrarouge réalisé sur poudre, avec le produit Merck à $36H_2O$ environ, nous montre une bande très large allant de 791 à 832 cm^{-1} et 5 bandes très fortes pour 899, 959, 982, 1061, 1626 cm^{-1}. L'interprétation en a déjà été donnée par DUVAL ET LECOMTE[7].

Paraperiodate de sodium

Ce sel de formule $Na_2H_3IO_6$, d'accord avec RAMMELSBERG[8], est anhydre et stable jusqu'à 207° où commence une décomposition lente donnant naissance à: de l'eau, de l'oxygène, de l'iodate, de l'iodure et de l'oxyde de sodium. Puis, au-dessus de 821°, l'iodate et l'iodure se subliment (Fig. 5).

Le spectre infrarouge ne nous a donné que des bandes faibles pour 761, 882, 916, 1150, 1206 et 1644 cm^{-1}.

Persulfate de potassium

La décomposition thermique a été étudiée par LEVI ET MIGLIORINI[9]. Le persulfate de potassium anhydre ne change pas de poids jusqu'à 230°. Il se décompose alors brusquement avec perte d'oxygène en fournissant du pyrosulfate de potassium, stable

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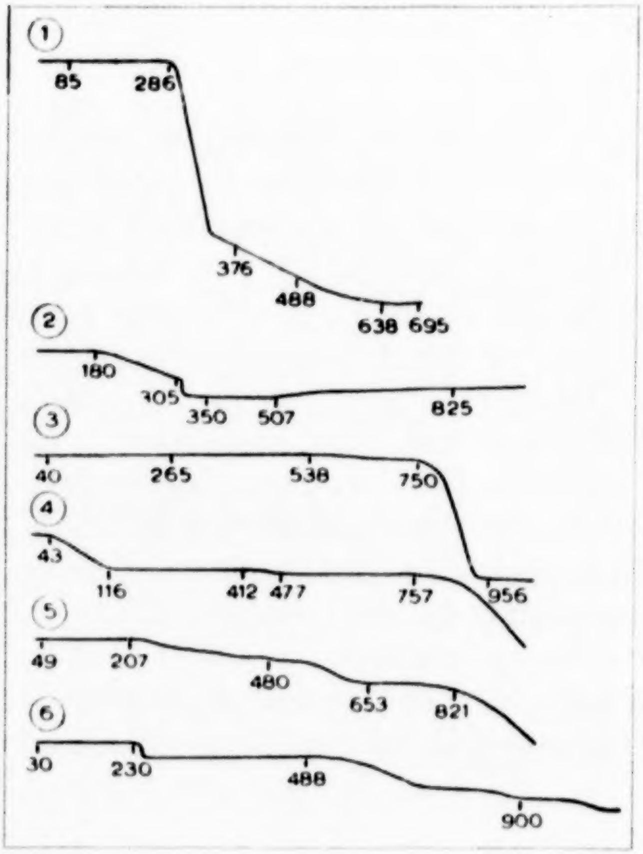
à son tour jusqu'à 488°. Après quoi, une nouvelle décomposition a lieu en anhydride sulfurique et sulfate de potassium, décomposition qui s'achève vers 900° (Fig. 6).

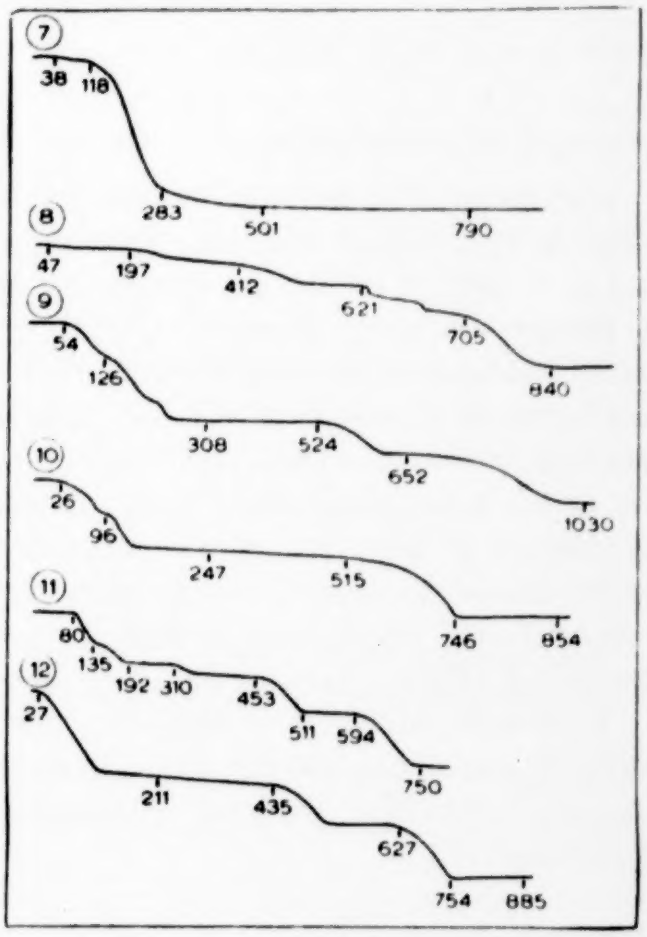
Le spectre infrarouge a déjà été fourni par PASCAL, DUVAL, LECOMTE ET PACAULT[10]; il donne les bandes: 900 (aF), 1059 (TF), 1254 (TF). Ces nombres sont d'accord avec ceux que nous avons reproduits plus récemment, à sec et en solution[11].

Chlorure d'aluminium

Le chlorure d'aluminium extrait d'un flacon neuf possède la formule $AlCl_3 \cdot 6H_2O$. Toutefois, la manipulation nécessaire pour le mettre dans le creuset lui fait gagner un peu d'humidité dont la perte jusqu'à 38° est signalée sur la courbe de thermolyse (Fig. 7). L'hexahydrate paraît stable entre 38 et 118°; après quoi, une hydrolyse et une déshydratation conduisent à l'oxyde Al_2O_3, assez rapidement jusqu'à 500°, puis excessivement lentement après. Vers 800° l'opération paraît terminée. PARRAVANO ET MONTORO[12] indiquent que cette transformation est complète à 180°, mais il n'en est rien avec notre mode de chauffage.



Figs. 1–6.



Figs. 7–12.

Les six molécules d'eau sont assurément de constitution et conduisent à une bande extrêmement large entre 808 et 858 cm^{-1} et à une bande fine à 1626 cm^{-1} (qui est peut-être due à l'humidité captée par le corps au moment de confectionner la cuve).

Pyrosulfate de sodium

Le produit que nous avons eu entre les mains se présentait sous forme de plaques quelque peu hygroscopiques qu'il n'est pas recommandé de peser à la sortie du flacon.

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La stabilité se manifeste jusque vers 197° (contrairement au sulfate acide de sodium $NaHSO_4$, qui n'est pas un étalon mais que nous avons examiné par comparaison; il perd de l'eau dès 43°). Le pyrosulfate, au-dessus de 197° perd de l'anhydride sulfurique jusque vers 800° et à partir de 840° apparait le palier horizontal du sulfate neutre Na_2SO_4. L'équation:

$$Na_2S_2O_7 \rightarrow SO_3 + Na_2SO_4,$$

n'a pas été vérifiée d'une manière rigoureuse et le point de fusion mesuré sur un échantillon sorti d'un flacon neuf est 147° (en désaccord avec les nombres trouvés par CAMBI ET BOZZA[13], qui donnent 400.9° et qui indiquent aussi qu'à cette température le produit n'est pas dissocié) (Fig. 8).

Le spectre infrarouge dans la région du sel gemme, s'accorde assez bien avec celui des corps renfermant l'ion du type X_2O_7 et accuse les bandes: 856 (F), 895 (f), 1040 (aF), 1060 (aF), 1074 (f), 1166 (TF), 1245 (TF) cm^{-1}.

Alun d'aluminium et d'ammonium

Il est permis de lui supposer la formule $NH_4[Al(H_2O)_2(SO_6H_4)_2]\cdot 6H_2O$, par analogie avec la formule expérimentale donnée pour l'alun de chrome. Toutefois, il faut le remarquer, cet alun est assurément un complexe plus imparfait dans le cas de l'aluminium que dans le cas du chrome. La courbe de thermolyse est reproduite sur la Fig. 9 jusqu'à 1030° et nous en avons recommencé des fractions pour interpréter commodément la nature des produits apparus suivant les paliers. Ceci dit, l'alun à $12H_2O$ dont 6 à l'état d'eau de cristallisation, est stable jusqu'à 54°. Il perd la totalité de son eau jusque vers 310°, en 3 étapes qui ne sont d'ailleurs pas très nettement séparées avec notre vitesse de chauffe, c'est-à-dire d'abord la perte des 6 molécules d'eau de cristallisation jusque vers 126°, puis la perte de 4 molécules d'eau combinée à l'acide sulfurique jusque vers 170°, enfin la perte de 2 molécules d'eau disposées aux extrémités de l'axe quaternaire de l'octaèdre de Werner. Il faut noter tout de suite que le produit figurant suivant le palier presque horizontal entre 308 et 524°, n'est pas le sel double $(NH_4)_2SO_4 + Al_2(SO_4)_3$, mais plutôt un complexe du type $NH_4[Al(SO_4)_2]$. En effet, le sulfate d'ammonium, d'après des expériences précédentes, aurait déjà disparu par sublimation et dissociation; ainsi pour début de sa décomposition, CASPAR[14] indique 355° et JÄNECKE[15] 357°. Dans notre expérience, le sulfate d'ammonium, par suite de l'ouverture du complexe, s'échappe entre 524 et 620° environ. Il reste alors du sulfate d'aluminium, $Al_2(SO_4)_3$, qui commence à se dissocier progressivement vers 652° et l'alumine apparaît dès 1030°.

Nous avons soigneusement vérifié que cette alumine était exempte d'ion SO_4^{-2}, que le sulfate d'aluminium était exempt d'ammoniac et que ce corps contenu dans le sel anhydre et dans le sel dodécahydraté correspondait bien aux formules annoncées.

Le spectre infrarouge, qui est d'ailleurs le même pour tous les aluns à 12 molécules d'eau, montre deux bandes très fortes pour 918 et 1017 cm^{-1}, relatives au groupement SO_4.

Sulfate de fer bivalent cristallisé

Les échantillons parfaitement verts et provenant d'un flacon neuf, ne contiennent pas 7 molécules d'eau mais des quantités voisines de 6 et sur la courbe de thermolyse

(Fig. 10), on observe que la perte de poids se produit dès la température ordinaire. Les 6 ou 7 molécules d'eau ne partent pas d'un seul coup et l'allure de la courbe dépend beaucoup de la vitesse de chauffage. On peut dire, en gros, que 3 molécules d'eau partent entre 26 et 96°, déjà avec oxydation partielle, que 3 autres molécules disparaissent entre 100 et 140° (quelques auteurs avant nous avaient donné 110–120 ou 160°). Le départ de la dernière molécule se fait en même temps qu'une altération profonde ne conduisant ni au sulfate de fer(II) anhydre, ni à un sulfate de fer(III) anhydre, sans toutefois qu'il y ait de palier très net. SAITO[16], par chauffage linéaire de 1° par minute, avait donné 540-550° pour le domaine d'existence de ce sulfate basique, qui pourrait s'écrire $2SO_3 \cdot Fe_2O_3$, corps déjà signalé. Il perd alors l'anhydride sulfurique et au-dessus de 720° commence le palier qui correspond à l'oxyde salin Fe_3O_4 (Fig. 10).

Le spectre infrarouge montre naturellement la bande très forte pour 1103 cm^{-1}, correspondant à la triple dégénérée du groupement SO_4, une bande large entre 812 et 828 cm^{-1}, puis des bandes beaucoup plus faibles pour 887, 988, 1016 et 1150 cm^{-1}.

Sel de Mohr

Le sel de Mohr sorti du flacon ne montre pas de perte d'humidité sur aucun de nos enregistrements. Il ne faut pas dépasser 80° pour le sécher. La perte des 6 molécules d'eau est compliquée par un léger départ d'ammoniac et une oxydation du fer, de sorte qu'entre 192 et 310°, on aboutit à $NH_4[Fe(SO_4)_2]$ correspondant en quelque sorte à l'alun anhydre, triple opération qui s'effectue jusque vers 453°. Il est impossible d'obtenir des paliers rigoureusement horizontaux. Entre 453 et 511° et entre 2 molécules du corps $NH_4[Fe(SO_4)_2]$, s'échappe une molécule de sulfate d'ammonium; il reste alors, sur un nouveau palier s'étendant de 511 à 594°, du sulfate de fer(III) $Fe_2(SO_4)_3$, qui n'est jamais rigoureusement pur. Alors commence la dissociation bien connue:

$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3,$$

mais comme on n'opère ni dans le vide, ni dans un milieu très réducteur mais dans l'air, le produit final, au-dessus de 750°, est l'oxyde Fe_3O_4.

Nous avons effectué des dosages répétés de fer correspondant à différentes températures de ce graphique (Fig. 11), mais il faut bien convenir que la thermolyse du sel de Mohr est une opération très compliquée et que les résultats manquent de netteté.

Le spectre infrarouge du sel de Mohr n'accuse pas la présence de la bande très forte de 1103 cm^{-1} correspondant au groupement SO_4, mais celle de 980 qui se retrouve chez les sulfates complexes. D'autre part, nous avons deux bandes fortes, l'une à 1385, l'autre à 1475 cm^{-1}, qui correspondent à l'ammoniac et à l'eau. C'est sans doute à cette dissimulation dans un complexe, que le sel de Mohr doit sa plus grande stabilité vis-à-vis de l'oxygène de l'air.

Alun de fer et d'ammonium

L'alun de fer et d'ammonium est un corps que l'on ne peut peser directement car il perd de l'eau dès la température ordinaire. Par suite, dans l'hypothèse de la formule $NH_4[Fe(H_2O)_2(SO_6H_4)_2] \cdot 6H_2O$, nous n'observons pas comme dans le cas de l'alun de chrome, trois paliers successifs pour le départ des 6 molécules d'eau de cristallisation, des 4 molécules d'eau combinée au soufre et des 2 molécules d'eau du complexe.

Cette eau part d'une manière continue jusque vers 211°. Là commence un palier rectiligne mais non horizontal, s'accordant assez bien avec la formule de l'alun anhydre, $NH_4[Fe(SO_4)_2]$, puis au-dessus de 435°, ce nouveau complexe se détruit à son tour, perdant du sulfate d'ammonium et nous tombons, comme dans le cas précédent, sur le sulfate de fer(III), se dissociant pour conduire à l'oxyde Fe_3O_4 (Fig. 12). Nous avons d'ailleurs tracé par comparaison, la courbe de dissociation du sulfate de fer(III) et, dans ce dernier cas, si la dissociation commence bien vers 600°, elle ne s'achève que plus haut, à 770° au lieu de 750°, avec la même vitesse de chauffe.

Le spectre infrarouge montre encore nettement que ce sel est un complexe; d'ailleurs, sa couleur et les expériences de migration d'ions l'indiquaient déjà. La bande forte de 1103 cm^{-1} du groupement SO_4 a disparu; elle est remplacée par deux bandes fortes à 993 et 1063 cm^{-1}. Signalons encore d'autres bandes fortes à 1373 et 1450 dues à l'ammoniac et à l'eau et des bandes très faibles à 871, 887, 1137, 1174 et 1216 cm^{-1}.

RÉSUMÉ

Nous avons étudié 12 substances pouvant servir d'étalons en analyse volumétrique, en insistant surtout sur la pyrolyse de 3 sels de fer.

SUMMARY

Twelve substances, which can be used as standards in volumetric analysis were studied, special attention being paid to the pyrolysis of the three iron salts among these substances.

ZUSAMMENFASSUNG

Es werden 12 Substanzen beschrieben, die bei der Mass-analyse als Standarde verwendet werden können, darunter 3 Eisensalze, deren Veränderungen durch Pyrolyse besonders betrachtet werden.

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4-(2-PYRIDYLAZO)-RESORCINOL AS A POSSIBLE ANALYTICAL REAGENT FOR THE COLORIMETRIC ESTIMATION OF COBALT, LEAD, AND URANIUM

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INTRODUCTION

The development of chromatography for use in the quantitative analysis of inorganic substances has led to the need for the re-examination of many of the recommended organic reagents used for final determination of cations by spectrophotometry. Hitherto, reagents were selected for ordinary analytical purpose on the grounds that they were very specific for the particular cation being estimated, but now that cations can be so readily separated by chromatographic methods from possible interfering cations, specificity of the reagent is not quite so important. By and large, the main requirements for reagents which can be used for the determination of individual cations such as occur after paper chromatographic separation are (1) high sensitivity, (2) water solubility to avoid organic solvent extraction, (3) reproducibility.

Many colorimetric reagents have been produced by coupling reactions following the diazotisation of benzenoid or naphthalenic nuclei. Relatively few having a pyridine base have been investigated however[1-4], and further investigation of the coupling reactions of phenols with pyridine bases has led to the synthesis of the reagent 4-(2-pyridylazo)-resorcinol (hereafter called PAR-4).

TSCHITSCHIBABIN[1,2] investigated the coupling of *o*-hydroxy-phenols, and LIU[3] carried out a detailed investigation into one of these compounds, 1-(2-pyridylazo)-2-naphthol (PAN-2). This investigation, however, was directed at deducing the structures of the metal-chelate lakes formed, rather than at the colorimetric properties of the reagent. A similar, but much less detailed, investigation was made into the dyestuff produced by coupling with resorcinol.

CHENG AND BRAY[4] later investigated the analytical properties of PAN-2, and have suggested its use as an indicator in the complexiometric titration of zinc, copper and cadmium with ethylenediaminetetracetic acid (EDTA). FLASCHKE AND ABDINE[5] have recommended a modified procedure which leads to the use of PAN-2 as indicator in the complexiometric titration of iron, copper, nickel, cobalt, zinc, cadmium and gallium. CHENG[6] has suggested a further procedure for the complexiometric titration of indium.

BUSEV[7] has studied the complexiometric titration of Bi with EDTA, using PAN as indicator, and CHENG[8] has also studied a similar technique for titration of Cu, Zn, Cd and Ni with EDTA.

Our investigation has shown that PAR-4 has outstanding possibilities as a highly sensitive, water-soluble reagent for the colorimetric estimation of cobalt, lead and uranium.

EXPERIMENTAL

Preparation of dyestuffs

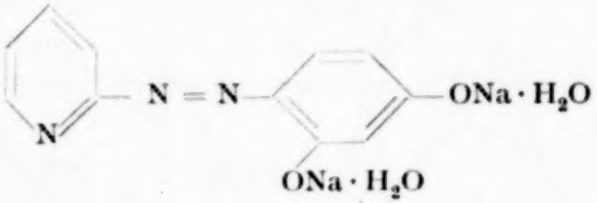
(*a*) ***Preparation of diazotate***[2]. (All reagents used were of AnalaR quality.) A solution of sodium ethylate was obtained by dissolving metallic sodium (1.2 g) in absolute alcohol (18.5 ml). 2-Amino pyridine (5 g) was dissolved in the minimum quantity of absolute alcohol (5 ml), and isoamyl nitrite (6 g) was added. The solutions were mixed and refluxed gently for 2–2$^1/_2$ h, the diazotate forming as a brown solid. Coupling reactions were then carried out directly, without isolation of the very unstable diazotate.

(*b*) *Coupling reactions*. All the phenolic compounds with which coupling was attempted were dissolved in absolute alcohol and mixed with the alcoholic diazotate solution. Carbon dioxide was then passed into the solution, which was cooled in an ice bath.

No product was isolated from the attempted coupling of pyridyl diazotate with 2-naphthol-6-sulphonic acid (Schäffer's acid), 2-naphthol-6,8-disulphonic acid (G-acid), 2-naphthol-3,6-disulphonic acid (H-acid), and 1-nitroso-2-naphthol-3,6-disulphonic acid (Nitroso-R-salt).

Coupling with resorcinol (8 g) in absolute alcohol (5 ml) resulted in the isolation of the disodium salt of PAR-4, the outstanding colorimetric properties of which are described in the next section. It was found that a far greater yield of dyestuff could be obtained by coupling the diazotate with resorcinol dissolved in the minimum quantity of water, followed by cooling in a refrigerator. The passing of CO_2 was also dispensed with, since the sodium salt was being isolated.

The crude PAR-4 (sodium salt) was isolated by filtration and thoroughly washed with ether in which it is only slightly soluble. All other impurities (resorcinol, etc.) being soluble in ether, were removed, and on drying *in vacuo*, pure dyestuff in the form of a brown, amorphous, slightly hygroscopic powder was obtained. Analysis showed that this was the disodium salt of PAR-4, together with two molecules of water of crystallization:



Theory: C = 44.3%, H = 3.76%, N = 14.0%, Na = 14.1%.
Found: C = 44.7%, H = 3.73%, N = 14.2%, Na = 15.6%.

(The authors are indebted to Messrs. WEILER AND STRAUSS of Oxford for these analyses).

The disodium salt of the dyestuff is soluble in water to give an orange solution; it is also soluble to some extent in absolute alcohol.

Colorimetric properties

Samples of aqueous solutions of AnalaR salts containing 0.5, 0.05, 0.005, and 0.0005 g of metal per litre were used to determine those ions which formed coloured chelates with the dyestuff. The technique used was that of HEISIG AND POLLARD[9]. Table I shows those ions which were found to give a colour:

TABLE I

Ion	*Colour*	*Ion*	*Colour*
Fe^{II}	Brownish-red	Cd^{II}	Pink-red
Fe^{III}	Brown	Sn^{II}	Pink → yellow
Co^{II}	Red	V^{V}	Purple
Ni^{II}	Red	Pb^{II}	Red
Cu^{II}	Red	U^{VI}	Red
Zn^{II}	Pink-red	Ti^{IV}	Red
		Rare earths	Red

The following cations failed to give a colour: Na^+, K^+, Ca^{+2}, Sr^{+2}, Ba^{+2}.

The sensitivities of the coloured complexes formed with Co^{II}, U^{VI}, and Pb^{II} have been investigated in considerable detail, and lead to the conclusion that PAR-4 is an excellent colorimetric reagent for the estimation of these metals.

Cobalt complex. The pH at which the optical density of the cobalt–dyestuff complex is a maximum, and the position of the maximum, were first determined. All measurements were made using a "Unicam" S.P. 500 spectrophotometer fitted with 1-cm silica cells. Buffer solutions for pH 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0 were obtained following the method of Clark and Lubs[10].

Aqueous solutions of the dyestuff (0.1 g in 100 ml, *i.e.* 1000 μg/ml) and AnalaR $CoCl_2{\cdot}6H_2O$ (12.38 μg Co/ml) were made up. Suitable proportions of the solutions were mixed, buffered to the requisite pH, and the optical density against a buffered dyestuff blank obtained over a range of wavelength from 450–620 mμ. Similarly the optical density of the aqueous dyestuff alone was obtained against a buffer blank in the range 330–520 mμ. The resulting spectra are shown in Fig. 1.

The dyestuff showed peak optical density at 410 mμ, over the pH range 7.0–9.0, and the complex showed peak optical density at 510 mμ over the same pH range. In all subsequent experiments on the cobalt complex the solutions were buffered at pH 8.0 for convenience.

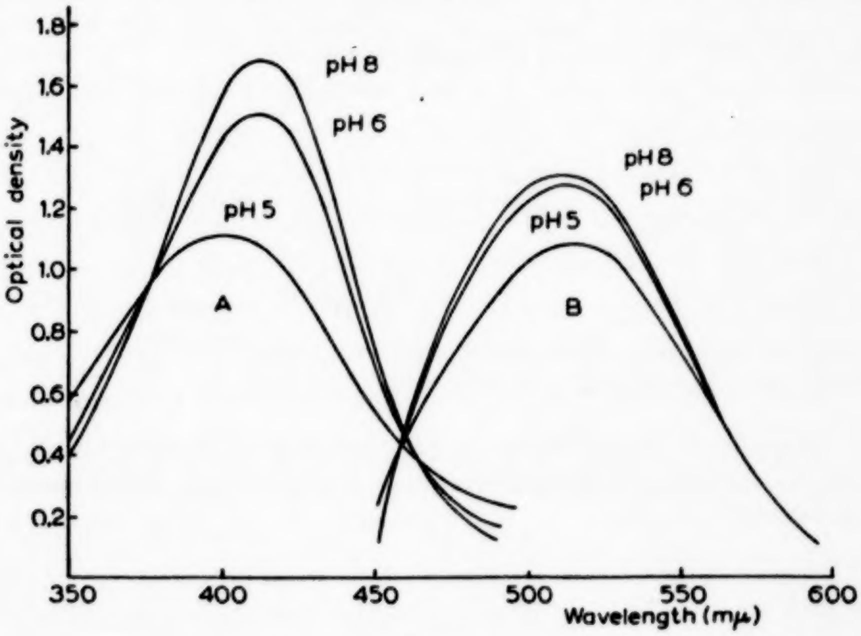


Fig. 1

A. Absorption spectrum of PAR-4. B. Absorption spectrum of cobalt complex.

The sensitivity of PAR-4 with cobalt was then determined as follows. A solution containing 10 μg/ml Co was obtained by dissolving 1.00935 g $CoCl_2{\cdot}6H_2O$ in 250 ml distilled water, and diluting a 10-ml aliquot to 1000 ml. A dyestuff solution of 1000 μg/ml was obtained by dissolving 0.25 g dyestuff in 250 ml distilled water. An optical blank was made up by mixing 1 ml of this dyestuff solution with 10 ml buffer pH 8.0, and diluting to 25 ml. Solutions of the coloured complex formed by mixing varying quantities of cobalt with a fixed quantity of dyestuff were obtained thus: x ml Co + 1 ml dyestuff + 10 ml buffer; diluted to 25 ml where:

$x=$	0.5	1.0	1.5	2.0	2.5	3.0	3.5	ml
i.e.	0.2	0.4	0.6	0.8	1.0	1.2	1.4	μg Co/ml

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In all these cases the amount of the dyestuff present was greatly in excess of that required for complete complex formation. The optical density of the above solutions against the prepared blank was determined at 510 mμ (the peak complex height). The results are shown in Table II:

TABLE II

μg Co/ml	0.200	0.400	0.600	0.800	1.000	1.200	1.400
O.D.	0.190	0.382	0.570	0.760	0.940	1.120	1.310

The plot of optical density *versus* concentration of cobalt in μg/ml is linear over the range 0–1.4 μg Co/ml, from which the sensitivity of the dyestuff with cobalt is found to be 0.93 O.D. units/μg Co/ml at 510 mμ. This sensitivity is far in advance of that of any of the standard colorimetric reagents for cobalt. Nitroso-R-salt, the most sensitive so far reported[11,12], has a sensitivity of approximately 0.5.

Uranium complex. Upon the addition of a uranium salt to a slightly alkaline solution of the dyestuff, a red colour is immediately produced. The peak height of the uranium complex was determined exactly as for the cobalt complex and was found to occur at 530 mμ (pH = 8.0), the reagent giving maximum absorption at 410 mμ. The sensitivity of the dyestuff with uranium was determined precisely as with the cobalt complex, using the following solutions:

Standard solution of AnalaR uranium acetate containing 1000 μg/ml uranium (*i.e.* 17.81 g salt/1000 ml).

Standard solution of PAR-4 (500 μg/ml).

Buffer pH 8.0.

The optical blank contained 2 ml dyestuff solution + 10 ml buffer, diluted to 25 ml. The test solutions contained *x* ml uranium + 2 ml dyestuff solution + 10 ml buffer, diluted to 25. The uranium solutions were measured from an "Agla" micrometer syringe. The optical densities of these solutions were measured at 530 mμ against the above blank. The results are tabulated in Table III.

TABLE III

μg/ml uranium	10.0	8.0	6.0	4.0	2.0	1.0
ml soln. and diln.	0.25_{25}	0.20_{25}	0.15_{25}	0.10_{25}	0.10_{50}	0.05_{50}
O.D. at 530 mμ	1.565	1.270	0.965	0.640	0.320	0.155

The sensitivity from this data is 0.160 optical density units/μg U/ml at 530 mμ, over the range 0–6.0 μg U/ml.

Again, this places PAR-4 well ahead of the recognised colorimetric reagents, both as regards sensitivity and water solubility. The most sensitive colorimetric reagent for uranium, dibenzoylmethane[13], is not water-soluble, and the sensitivities of the water-soluble reagents (salicylamidoxime[14], sulphosalicylic acid[15]) are less than that of PAR-4.

Lead complex. **Following the methods used for the cobalt and uranium complexes, the**

maximum absorbance for the lead complex was found to occur at 520 mμ. The colour of the complex was found to have maximum intensity when buffered to pH 10.0.

The sensitivity of PAR-4 with lead was found as in the previous cases. The following solutions were made up:

Standard solution of $Pb(NO_3)_2$ AnalaR, containing 1000 μg Pb/ml (*i.e.* 1.5990 g salt/1000 ml).

Standard solution of dyestuff containing 500 μg/ml.

Buffer solution pH 10.0.

To a 25-ml graduated flask was added a known amount of standard Pb solution (measured from an "Agla" micrometer syringe) + 2 ml dyestuff + 10 ml buffer. The mixture was diluted to 25 ml with distilled water, and the optical density measured at 530 mμ against a dyestuff + buffer blank. The results are tabulated in Table IV.

TABLE IV

μg Pb/ml	2.0	3.0	4.0	5.0	6.0	7.0
ml solution	0.10	0.15	0.20	0.25	0.30	0.35
O.D. at 520 mμ	0.348	0.514	0.684	0.860	1.020	1.196

This data gives the sensitivity as 0.171 optical density units/μg Pb/ml, over the range 0–5.0 μg Pb/ml.

A search of the literature has shown that no water-soluble colorimetric reagents for the estimation of lead have been reported, the most used method being estimation with dithizone following extraction with CCl_4.

GENERAL

Since PAR-4 gives coloured chelate compounds with many cations (see Table I) it is necessary to remove these ions before colorimetric estimation is possible. This may be achieved by several methods; in this laboratory interfering cations have been removed from lead solutions by paper chromatography, followed by determination of lead with PAR-4. Details of this procedure will be given in a later publication.

Investigations of the structures and stability constants of the metal chelate complexes of PAR-4 are at present in progress by spectrophotometric, polarographic and pH measurements. It is hoped to publish these results in a further paper.

The reagent 1-(2-pyridylazo)-4-phloroglucinol has also been synthesized, and its analytical properties are under investigation.

ACKNOWLEDGEMENTS

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SUMMARY

4-(2-Pyridylazo)-resorcinol has been synthesized, and its uses as an analytical reagent for the colorimetric estimation of cobalt, uranium and lead have been investigated. It has been shown to be the most sensitive reagent for the colorimetric estimation of cobalt, the most sensitive water-soluble reagent for the colorimetric estimation of uranium, and the first published water-soluble reagent for the colorimetric estimation of lead.

RÉSUMÉ

La pyridyle-2-azo-4-résorcine est proposée comme réactif analytique pour le dosage colorimétrique du cobalt, de l'uranium et du plomb. C'est un réactif particulièrement sensible.

ZUSAMMENFASSUNG

Es wurde gefunden, dass das Pyridyl-2-azo-4-resorcin ein äusserst empfindliches Reagens für die colorimetrische Bestimmung von Kobalt, Uran und Blei darstellt.

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THE ANALYSIS OF ZIRCONIUM-THORIUM BINARY ALLOYS

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INTRODUCTION

Complexometric titrations were considered for the analysis of this type of alloy because both zirconium and thorium can be determined individually by this technique. Experience with complexometric titrations for these elements has shown that the most satisfactory ones employ xylenol orange as indicator. The direct titration of zirconium is not very suitable because of hydrolysis difficulties, except in solutions approximately *N* in mineral acid. Under these conditions the determination of zirconium is possible directly in the presence of thorium since the thorium-EDTA complex is not formed. A back titration procedure is widely used for the determination of zirconium; this employs either bismuth or thorium as the titrant of the excess of ethylenediaminetetraacetic acid (EDTA) to the xylenol orange end-point[1]. With this procedure it may be possible to prevent interference from thorium by the use of a suitable masking agent. In the analysis of bismuth-thorium alloys, for example, **Bacon and Milner**[2] succeeded in masking up to 100 mg of thorium with sulphate ions in the complexometric titration of bismuth. Both these approaches have been examined and the results are described in this paper.

EXPERIMENTAL

The direct titration of zirconium in the presence of thorium

KÖRBL AND PRIBIL[3] have reported the direct titration of zirconium with EDTA in hot normal nitric acid solutions using xylenol orange as indicator. Due to slight fading at the end-point, we obtained final titres slightly lower than the theoretical value. It was found that if, after titration to the end-point, sufficient ammonium hydroxide was added to neutralise about 80% of the nitric acid, the pink colour of the indicator was restored and a further small titration with EDTA could be carried out. The final titre was then correct for small amounts of zirconium, but slightly low for amounts greater than about 30 mg of zirconium. Under these less acid conditions, however, the tolerance for thorium proved much lower, amounts as low as 20–30 mg causing serious interference. Fluoride and sulphate ions interfered badly, no titration being possible in the presence of as little as 2–3 mg of fluoride and 100 mg of sulphate. Since the use of either hydrofluoric acid or sulphuric acid or both may be essential for the solution of alloy samples, further study of this direct titration method was discontinued.

Determination of zirconium and thorium with EDTA by back titration with bismuth

According to KÖRBL AND PRIBIL[3], bismuth can be titrated directly with EDTA in solutions between pH 1 and 3 using xylenol orange as indicator. At higher pH values, hydrolysis of bismuth causes difficulties. The reverse titration of EDTA with bismuth can be carried out in solutions up to pH 3.7, although the colour change of the indicator is sluggish at pH values greater than 3.5. Using bismuth for the titration of excess of EDTA, zirconium can be determined between pH 1.2 and 3.5, whereas the smaller pH range of 2.3 to 3.7 is applicable in the case of thorium. For quantitative results for zirconium, the excess of EDTA must be added to a fairly acid solution (*e.g.* $> 1.0N$ in nitric acid). In the thorium determination a slight positive error occurs at pH values less than 2.3, the sluggish colour change at the end-point possibly accounting for this error. The titration of known mixtures of thorium and zirconium resulted in the correct total being obtained when the titration was carried out between pH 2 and 3.

The behaviour of most other cations in this back titration procedure can be predicted from the stability constant data available in the literature. However, the behaviour of anions cannot be assessed with the same certainty and is best determined experimentally. The number of anions of direct interest in this work could be limited to about two, since the only useful solvents for zirconium metal and some of its alloys are a mixture of hydrofluoric and nitric acids or boiling concentrated sulphuric acid. Some knowledge of the effects of both sulphate and fluoride ions on the determination of thorium and zirconium was essential. From previous work the effect of sulphate ions on the determination of thorium was known to be serious[2]. Their effect on the determination of zirconium was found to depend on whether the sulphate was present before or after the addition of the EDTA. The addition of small amounts of sulphuric acid to a solution of zirconium in $2N$ nitric acid before the excess of EDTA caused low recoveries. However, large amounts of sulphate ions could be added after the complexation of the zirconium with EDTA with negligible effect on the recovery.

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The complexation of thorium by sulphate ions proved to be of potential value for the direct determination of zirconium in the presence of thorium. Experiments showed, for example, that amounts of thorium up to at least 100 mg could be completely masked under favourable conditions. For the determination of zirconium under such conditions, solutions adjusted to the bottom of the previously reported pH range of 1.2 to 3.5 had to be employed. This low pH proved necessary because of difficulty in detecting the end-point visually at the higher values. An ammonium sulphate concentration of 2–3 g in 100 ml of solution proved very convenient and increasing it to greater values was found to serve no useful purpose.

Fluoride ions were found to affect adversely the determination of both thorium and zirconium, although they had little influence in the titration of EDTA with bismuth. As little as 1 mg of fluoride as sodium fluoride caused the masking of several milligrams of either thorium or zirconium. However, this effect could be nullified by the addition of beryllium to preferentially combine with the fluoride ions. The amount of beryllium needed to mask a certain amount of fluoride was found to depend on the pH of the solution. Thus in the determination of zirconium at pH 1.2, 1 ml of 50% w/v beryllium nitrate solution could mask 20 mg of fluoride, whilst at pH 3 it could mask at least 100 mg of fluoride, and similarly in the thorium determination.

Determination of thorium and zirconium in the same solution

From the results of the previous section it is possible to determine the total content of thorium plus zirconium and also the amount of EDTA combined with the thorium by preferential complexation with sulphate ions. Before these titrations could be applied in metallurgical analysis, however, it was necessary to prove them by analysing solutions of various compositions. Suitable mixtures of thorium and zirconium were prepared from 0.02*M* solutions of thorium nitrate and zirconium nitrate. Sufficient 0.02*M* EDTA was added to each solution to complex the thorium and zirconium and provide a small excess. After adjusting pH to 2.5–2.7, the EDTA in excess was determined by titration with 0.02*M* bismuth nitrate. Then 2–3 g of ammonium sulphate was dissolved in the solution, followed by the addition of nitric acid to lower pH to 1.2 to 1.3. The back titration with bismuth was then continued to determine the amount of EDTA liberated from the thorium complex. From these titres the composition of the thorium–zirconium mixture could be calculated and typical results are given in Table I.

TABLE I

THE ANALYSIS OF THORIUM–ZIRCONIUM MIXTURES
(all solutions were exactly 0.02*M*)

Taken (ml)		*EDTA added*	*Back titraton with Bi (ml)*		*Found*		*Error*	
Th	*Zr*	*ml*	*pH 2.5*	*pH 1.3*	*Th*	*Zr*	*Th*	*Zr*
25.00	1.00	26.50	0.51	25.51	25.00	0.99	Nil	+0.01
25.00	1.00	26.50	0.49	25.48	24.99	1.02	—0.01	+0.02
20.00	5.00	25.50	0.51	10.50	19.99	5.00	—0.01	Nil
10.00	10.00	20.50	0.49	10.48	9.99	10.02	—0.01	+0.02
5.00	20.00	25.50	0.49	5.50	5.01	20.00	+0.01	Nil

It was shown that both thorium and zirconium determinations could be carried out directly at a 25/1 molar ratio of Th to Zr and Zr to Th respectively with a standard deviation of ± 0.01 ml of $0.02M$ solution. Therefore, in order to obtain an accuracy of $\pm 1\%$, it can be calculated that the lowest weight percentages of each metal are 10% thorium in zirconium-rich alloys and 1.6% zirconium in thorium-rich alloys. For the analysis of actual alloys it was considered preferable to increase these limits to about 20% for thorium and 5% for zirconium respectively. For other alloy compositions less direct methods involving some form of preliminary separation would have to be developed. The separation of thorium and zirconium need not be perfect, as long as the ratio of these constituents was reduced to a satisfactory value so that the EDTA procedures become applicable.

Separation and determination of small amounts of thorium

The available chemical methods for the separation of thorium from zirconium are very limited and that involving the precipitation of thorium as its insoluble fluoride proved to be the only approach applicable to this problem. In preliminary experiments the precipitation of thorium fluoride from nitric acid solutions was carried out by the addition of ammonium fluoride. With 5-mg amounts of thorium, the recovery was slightly low, but quantitative recoveries were obtained with larger amounts. Because of this behaviour, lanthanum was added to the solution to improve the recoveries at the lower levels. This procedure was tested on the recovery of thorium in the presence and absence of zirconium and full recoveries were obtained for 4.5- to 50-mg amounts of thorium in the presence of 500 mg of zirconium.

Separation and determination of small amounts of zirconium

Mandelic acid[4,5] and its derivatives are applicable to the precipitation of zirconium in the presence of thorium. The *p*-bromo derivative[6] is better than mandelic acid for the precipitation of small amounts of zirconium; it is also more satisfactory in the presence of sulphate ions. The application of this reagent was therefore studied because the presence of sulphuric acid in the sample solution was anticipated since the only effective way of removing fluoride ions from zirconium involves heating to strong fumes of sulphuric acid. Quantitative results were obtained for the determination of 0.5 to 2.5 mg amounts of zirconium in the presence of 100 mg amounts of thorium.

THE ANALYSIS OF ALLOYS

Solution procedure

A mixture of nitric and hydrofluoric acids was found to be a suitable solvent for the majority of alloys in this system. The best procedure consisted of the transference of a suitable weight of sample to a platinum dish, followed by the addition of 10 ml of nitric acid (sp. gr. 1.42) and 4 to 5 drops of 40% hydrofluoric acid and gentle warming of the dish and its contents. The use of a platinum lid to cover the dish was found to be essential to reduce losses of acid by evaporation and then only occasional additions of nitric acid were necessary to maintain the volume of this acid at the desired level. Most samples dissolved readily by this procedure but some difficulty was encountered with samples containing between 70 and 90% of zirconium. With these samples extreme caution was needed during the warming process, otherwise spontaneous combustion occurred with the formation of hard globules of oxide very resistant to solution. On completion of the solution of the sample in the nitric–hydrofluoric acid mixture, 20 ml of 60% perchloric acid was added to the platinum dish followed by evaporation to fumes of this acid. After cooling, the sample solution was quantitatively transferred to a 150-ml beaker with water washings and any small residue was dissolved in nitric acid. Then the solution was evaporated to fumes of perchloric acid again and the beaker was covered and the boiling of the acid continued to produce a clear solution. Next the beaker was uncovered and heating was continued to reduce the volume of perchloric acid to about 10 ml. After cooling, the solution was diluted with 25 ml of $5N$ nitric acid and finally made up to volume in a 100-ml volumetric flask.

Experience showed that the relative ease of solution depended on the zirconium content of the alloy. There was no difficulty with samples of low zirconium content. Moreover, the resultant perchloric acid solution could be evaporated to dryness and complete solution of the residue could be effected in $5N$ nitric acid. With alloys of high zirconium content, however, the position was less satisfactory and it was found to be necessary to limit the weight of sample to not more than about 250 mg. With greater sample weights a deposit was formed on fuming with perchloric acid and re-solution of this material proved extremely difficult unless it was heated with fuming sulphuric acid. This same type of deposit could also be formed on taking sample weights less than 250 mg by carelessness in the evaporation of perchloric acid and by removal of too much of this acid.

METHODS OF ANALYSIS

Reagents required

0.02M Bismuth nitrate solution. Dissolve 4.180 g of high purity bismuth metal in 100 ml 25% v/v nitric acid, boil the solution vigorously, cool and dilute to 1 l in a graduated flask.

0.02M EDTA solution. Dissolve 7.45 g of the di-sodium salt of the ethylenediaminetetraacetic acid di-hydrate in 1 l of water. Standardise against the $0.02M$ bismuth nitrate solution using xylenol orange indicator at pH 1.2–3.0.

2% p-Bromo-mandelic acid solution. Dissolve 10 g of the acid by warming with 500 ml of water, cool to room temperature and filter.

20% Ammonium fluoride solution. Dissolve 100 g of the A.R. salt in 500 ml of water, filter and keep in a polythene bottle.

1% Ammonium fluoride wash solution. Dilute 25 ml of 20% ammonium fluoride solution to 500 ml with 1% v/v nitric acid.

0.1% Xylenol orange solution. Dissolve 100 mg of the dye in 100 ml of water.

Ammonium sulphate, hydrofluoric acid and all other reagents of A.R. quality.

De-ionised water should be used throughout.

Apparatus required

Platinum dishes (50 ml capacity) with covers,
50-ml "Lusteroid", centrifuge tubes,
Polythene stirring rods,
M.S.E. Major centrifuge,
Burettes, pipettes and graduated flasks, all grade "A" quality.

Procedure

Solution of alloys (See above)

Preliminary examination. Take an aliquot to contain not more than 40 mg of zirconium-rich alloys or 100 mg of thorium-rich alloys and transfer to a 250-ml beaker. Add 25 to 30 ml of $0.02M$ EDTA solution and dilute to 150 ml. Introduce pH electrodes and a stirrer. Add 1 drop of 0.1% xylenol orange solution and adjust to pH 2 by the addition of ammonia. If the solution is pink, add enough 0.02*M* EDTA solution to turn the indicator yellow and provide a small excess. Finally adjust to pH 2.6–2.8 with dilute ammonia. Add 3 ml 50% w/v beryllium nitrate solution, readjust the pH and back titrate with 0.02*M* bismuth solution until the indicator turns pink. Next add 2–3 g ammonium sulphate and concentrated nitric acid dropwise until the solution is in the range pH 1.2–1.3. Continue to back titrate with 0.02*M* bismuth solution until the indicator again turns pink. Titrate slowly when approaching the end-point.

Calculate the thorium content from the difference in the bismuth titres and the zirconium content from the total EDTA added minus the total bismuth added.

1 ml 0.02*M* EDTA solution ≡ 4.642 mg Th or 1.824 mg Zr. If, from the preliminary examination, the alloy contains 20–95% thorium and 5–80% zirconium repeat the above procedure on more convenient aliquots of the sample solution to improve the accuracy of the results.

For alloys with < 20% thorium. Take an increased sample weight up to 500 mg and dissolve in nitric–hydrofluoric acid mixture. Transfer the solution to a 50-ml "Lusteroid" centrifuge tube and with washings make up to 25–30 ml. Add 20 mg of lanthanum carrier and 10 ml 20% ammonium fluoride solution. Stir with a polythene rod and spin in a centrifuge for 10 min. Discard the supernate, wash the precipitate with 20 ml of ammonium fluoride wash solution and again spin in a centrifuge for 5 min. Discard the supernate and transfer the precipitate into a 150-ml beaker with water washing. Rinse the centrifuge tube with 5 ml of concentrated nitric acid and more water. Add 5 ml 60% perchloric acid to the suspension in the beaker and evaporate to fumes of this acid. Continue the evaporation until the residue is almost dry. Dissolve the residue in dilute nitric acid, dilute to 100 ml with water, then add excess 0.02*M* EDTA solution and titrate as described in the preliminary examination.

For alloys with < 5% zirconium. Take an aliquot of the sample solution containing up to 100 mg of sample and add 1–2 ml of concentrated sulphuric acid. Evaporate carefully to dryness and gently heat the sides of the beaker with a bunsen flame to remove any condensed sulphuric acid. Cool the beaker, dissolve the residue in 20 ml 20% v/v hydrochloric acid by gentle heating and add 20 ml 2% *p*-bromo-mandelic acid solution. Cover with a watch glass, heat to boiling and then allow the solution to stand for 1 h at 90–95°. Filter the solution through a 9-cm Whatman No. 40 paper and wash the precipitate and beaker with water. Place the paper and precipitate back into the original beaker, cover it with a watch glass after adding 5 ml fuming nitric acid and heat. When the acid has nearly all evaporated, add a further 5 ml of nitric acid and 2–3 ml of perchloric acid and evaporate nearly to dryness. Dissolve the residue in 5 ml 5*N* nitric acid and dilute to 25 ml. Add excess 0.02*M* EDTA, 1 drop of 0.1% xylenol orange solution, 200–300 mg of ammonium sulphate and back titrate with 0.02*M* bismuth solution at pH 1.2–1.3.

RESULTS AND CONCLUSIONS

The methods for the analysis of binary alloys were tested by applying them to samples covering the complete composition range from 1–99% of thorium and of

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zirconium respectively. The results obtained together with some statistics on the reproducibility of the methods are given in Table II. The reproducibilities of the separation methods for alloys with less than 5% thorium and 20% zirconium respectively were found to be satisfactory on several samples and the methods proved to be very reliable. Only one sample was available for testing the direct method. However, the standard deviations obtained confirmed the suitability of this method.

TABLE II

RESULTS FOR THE ANALYSIS OF THORIUM–ZIRCONIUM BINARY ALLOYS

Nominal composition	*Method employed*		*Composition by analysis*	
			% Thorium	*% Zirconium*
1. 1% Zr	Fluoride pptn.		98.56	0.971 ± 0.006
2. 3% Zr	Fluoride pptn.		95.80	3.03 ± 0.04
3. 4% Zr	Fluoride pptn.		—	4.12 ± 0.011
4. 70% Zr	Direct	1)	30.18 ± 0.15	69.57 ± 0.012
		2)	30.11 ± 0.19	69.63 ± 0.08
5. 15% Th	*p*-Bromo-mandelate		15.34	84.44
6. 5% Th	*p*-Bromo-mandelate		4.99	—
7. 1% Th	*p*-Bromo-mandelate		1.03 ± 0.03	—

SUMMARY

Thorium–zirconium binary alloys are analysed by complexometric procedures. For alloys containing more than 20% thorium or 5% zirconium by weight, the sum of the constituents is obtained by a back titration procedure at pH 2.6–2.8 with bismuth nitrate using xylenol orange as indicator. Thorium is then masked with sulphate and the liberated EDTA is titrated with bismuth at pH 1.2–1.3. For alloys containing less than 20% of thorium, thorium fluoride is precipitated on lanthanum fluoride to effect its separation before titration. For alloys containing less than 5% of zirconium, the zirconium is separated by precipitation with *p*-bromo-mandelic acid.

RÉSUMÉ

On propose des méthodes complexométriques pour l'analyse d'alliages binaires thorium–zirconium. On peut obtenir la somme thorium + zirconium par titrage indirect au moyen de nitrate de bismuth, en présence d'orange de xylénol. On masque ensuite le thorium et on titre l'acide EDTA libéré. (Si < 20% de thorium: on le sépare préalablement comme fluorure. Si < 5% de zirconium: on le sépare préalablement à l'aide de l'acide *p*-bromo-mandélique.)

ZUSAMMENFASSUNG

Es wird eine komplexometrische Methode zur Analyse einer binären Legierung von Thorium–Zirkonium beschrieben. Man bestimmt zunächst die Summe Thorium–Zirkonium durch indirekte Titration mit einer Lösung von Wismutnitrat und Xylenol-Orange als Indikator. Thorium wird dann maskiert und die frei gewordene EDTA mit Wismut titriert. Bei weniger als 20% Thorium wird dieses vor der Titration als Thoriumfluorid abgeschieden. Bei weniger als 5% Zirkonium wird dieses mit *p*-Brommandelsäure abgetrennt.

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DIRECT FLAME-PHOTOMETRIC DETERMINATION OF CALCIUM IN SOIL AND PLANT EXTRACTS, WATER AND SERUM

WITH SPECIAL REFERENCE TO SODIUM, POTASSIUM AND PHOSPHATE INTERFERENCE

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The increasing use of flame photometry in recent years for the determination not only of the alkali metals, but also of calcium, justifies an investigation of the main interfering agents in the determination of the latter, with a view to exploring the possibilities of its application to the routine analysis of such common materials, as soils, plants, water and serum.

BARNES *et al.*[1] state that the presence of sodium causes an apparent increase in calcium content. EDGCOMBE AND HEWETT[2], investigating the determination of calcium in coal ash and coke ash, reported interference effects due to sodium, potassium and phosphate, among others, in the determination of calcium oxide. The interference effect of aluminium on calcium is of importance, especially with respect to soil analysis[3]. The presence of bicarbonate in natural waters is known to cause serious depression of calcium emission[4]. Since these effects at certain, not unusual, concentrations may be very significant, it is generally considered necessary for calcium determination with single-cell, filter flame photometers, to free it first from interfering agents by precipitation as oxalate. The precipitate is then dissolved in dilute perchloric acid and finally sprayed.

The aim of this work was to investigate the possibilities of calcium determination by direct spraying, without the preliminary precipitation as oxalate.

Physical sources of error, such as (a) fluctuation of the spraying rate, (b) changes of air and gas pressures, (c) variation of flame temperature, and (d) insufficiency of the filters, were considered to be outside the scope of this work. They have been discussed, among others, by FOX[5] and ROBINSON AND OVENSTON[6]. Impurities and the so-called "inert materials" which affect the viscosity of the test solutions have been dealt with by CATON AND BREMNER[7].

EXPERIMENTAL

Apparatus

An EEL flame photometer (Evans Electroselenium Ltd., Harlow, Essex, England) was used throughout this work[8]. The results, therefore, may not apply to other instruments, certainly not to those based on the internal standard technique. This is essentially a single-cell instrument using butane gas–air mixture. The optical sodium and potassium filters used are of gelatine cemented between glass, whereas the calcium filter is of the interference type. The relative over-all spectral responses of the filter–photo-cell combination for sodium and potassium have been reported by COLLINS AND POLKINHORNE[8], those for calcium are shown in Fig. 1.

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All analyses were carried out in duplicate. To ascertain the reproducibility of the results, flame-photometric scale readings were first made serially and then repeated, the scale adjustment being re-checked against standard solutions during the repeat tests.

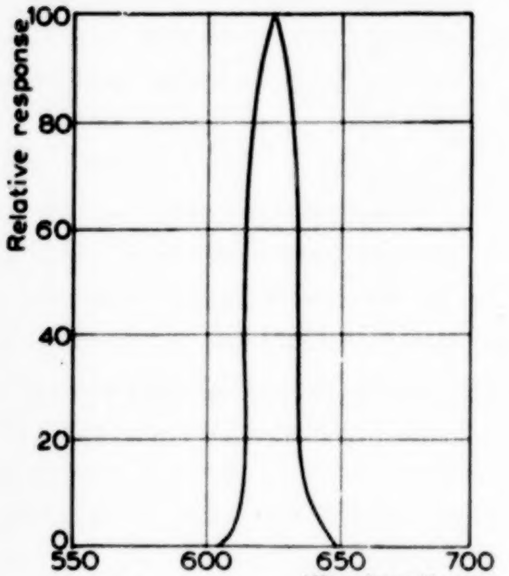

Fig. 1. Combined cell and filter response for calcium. (Courtesy of Evans Electroselenium Ltd., Harlow, Essex, Great Britain)

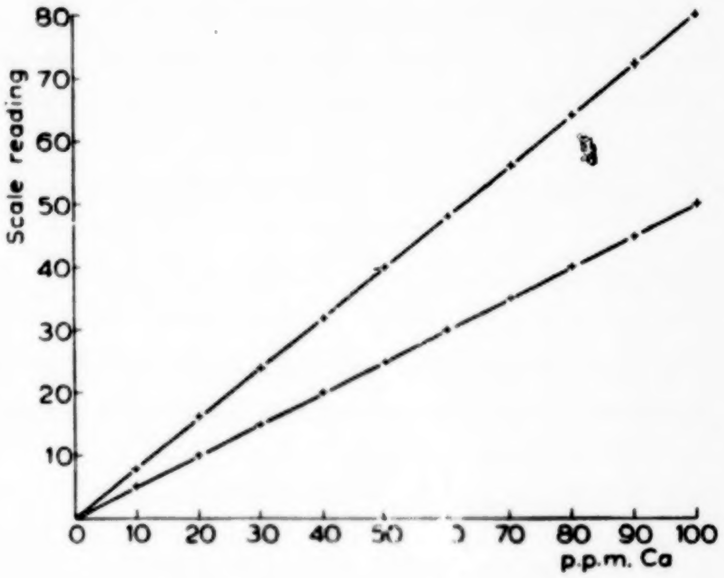

Fig. 2. Ca calibration curves at two different potentiometer settings.

Reagents

AnalaR reagents and demineralized water (containing about 0.5 p.p.m. of total salts as sodium chloride) were used throughout.

Standard solutions: A stock solution of 10,000 p.p.m. of calcium was made by dissolving 24.970 g of pure calcite (Iceland spar–$CaCO_3$) in a minimum of hydrochloric acid and making up to 1 l with water. Similarly the sodium and potassium stock solutions each containing 10,000 p.p.m. of the metal were prepared by drying their chlorides at 110° to constant weight, dissolving 25.422 g and 19.069 g respectively and making up to 1 l. For the preparation of a stock solution containing 1000 p.p.m. of phosphate, 1.400 g of ammonium monohydrogen phosphate, $(NH_4)_2HPO_4$, were dissolved in water and brought to 1 l.

Neutral N ammonium acetate solution[9]: Approx. 2*N* NH_4OH from conc. NH_4OH and 2*N* acetic acid from glacial acetic acid were prepared. The two solutions were mixed and the pH adjusted to 7.0 with a glass electrode. The solution should be kept in a stoppered bottle.

Calibration curve for Ca

Fig. 2 shows the instrument's two calibration curves for calcium made at two different potentiometer settings. Both lines are straight, which is evidence of the linear response of the photocell to the calcium emission in this range.

Effect of sodium on calcium

Using the calcium and the sodium stock solutions, a series of solutions was prepared containing from 0 to 5,000 p.p.m. of sodium, together with 100 p.p.m. of calcium. After adjusting the galvanometer spot to read zero for demineralized water and 50 for the sodium-free solution containing 100 p.p.m. of calcium, the series was sprayed and the amount of calcium thus found was recorded.

TABLE I

ERROR IN DETERMINING 100 p.p.m. OF CALCIUM IN THE PRESENCE OF SODIUM BY FLAME PHOTOMETER

Sodium present p.p.m.	*Calcium found p.p.m.*	*Error %*
50	102.0	+ 2.0
100	103.8	+ 3.8
200	106.8	+ 6.8
300	108.5	+ 8.5
500	113.0	+ 13.0
1,000	121.0	+ 21.0
2,000	136.7	+ 36.7
3,000	150.0	+ 50.0
4,000	163.5	+ 63.5
5,000	175.0	+ 75.0

It can be observed from Table I and Fig. 3 that the positive error caused by the presence of sodium is considerable, amounting to 75% for 5,000 p.p.m. of sodium.

Effect of potassium on calcium

A series of solutions containing from 0 to 5,000 p.p.m. of potassium together with 100 p.p.m. of calcium were likewise prepared from the stock solutions and similarly sprayed, adjusting the galvanometer spot to read 80 for the potassium-free solution containing 100 p.p.m. of calcium.

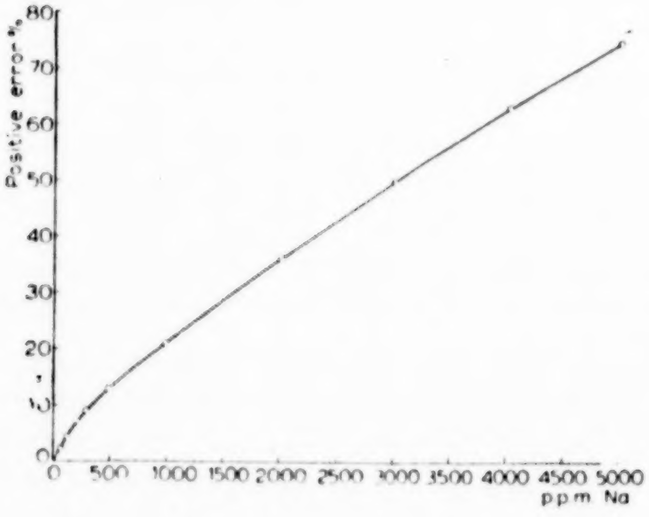

Fig. 3. Effect of sodium on 100 p.p.m. calcium.

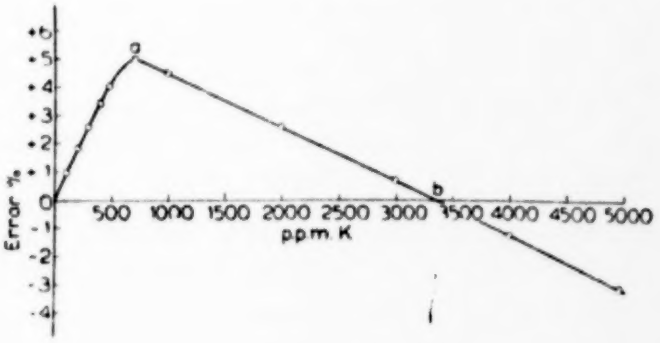

Fig. 4. Effect of potassium on 100 p.p.m. calcium.

Fig. 4 indicates that the error due to the effect of potassium on calcium differs radically in magnitude from that due to sodium and, above a certain concentration, in sign too. That the interference of sodium is relatively much greater in magnitude than that of potassium, may be explained, among other factors, by the following facts:

(a) The relative intensity of sodium measured at 5893 Å is 10,000, whereas it is 2,000 for potassium measured at 7670 Å[10]. The increment of flame background intensity due to sodium is, therefore, 5 times larger than that due to potassium. The relative intensity is defined as 100 divided by the number of p.p.m. of the element required to give a photometric response equal to 0.5% of the flame background.

(b) The sodium doublet (5890 and 5896 Å), being much closer to the calcium bands (6030, 6240 and 6480 Å) than the potassium doublet (7660 and 7690 Å), stands a greater chance of benefitting from the insufficiency of the calcium filter.

As an attempt to explain the unique behaviour of the potassium effect on calcium when it comes to the sign of the error, it may be assumed that, when potassium is sprayed together with calcium, two opposed factors come into play:

(i) an emission-intensifying effect due to the general increase in flame background, etc., and

(ii) an emission-suppressing effect caused by self-absorption of energy within the flame, anion interference, etc.

At low concentrations of potassium, effect (a) evidently becomes increasingly dominant, giving a maximum error of + 5% at 700 p.p.m. of potassium, after which the equilibrium turns more and more in favour of effect (b). At 3,350 p.p.m. of potassium, the two effects apparently just cancel each other out, and the same amount of calcium is read with or without this amount of potassium. Larger concentrations of potassium proved to give a negative error, indicating increasing dominance of effect (b).

The phenomenon of self-absorption of energy within the flame has been discussed by several authors. HARRISON *et al.*[11] point out that "an interesting situation arises when radiation emitted by an assemblage of atoms is divided into two regions, one at a higher and one at a lower temperature. Such a situation may exist . . . in which the atoms at the center . . . are at a higher temperature while the ones at the periphery are at lower temperatures. The spectral lines which originate at the higher energy levels will be emitted by the high temperature part of the assemblage with relatively higher intensities than the lower temperature part, but before this radiation can leave (the source) it must pass through the region of low-temperature atoms . . . and the radiation is absorbed."

"The diminution (of intensity) may be so great, that the lines actually are weaker than the continuous background."

The phenomenon is further discussed by HARVEY[12] who states that "as the concentration of the atoms in the discharge increases and the amount of atoms in the cold vapor correspondingly increases, the probability of absorption becomes greater . . . The absorption may occur partly in the discharge itself and partly in the cooler vapor

TABLE II

EFFECT OF WORKING AIR-PRESSURE ON THE POTASSIUM INTERFERENCE WITH 100 p.p.m. CALCIUM

Working air-pressure g/cm²	*Corresponding aspirat. rate ml/sec*	*Scale reading of K-free 100 p.p.m. Ca*	*Max. positive error %*	*p.p.m. K producing max. positive error **	*p.p.m. K producing zero error ***
562	0.0487	40.0	+ 4.5	625	3150
703	0.0550	50.0	+ 5.0	700	3350
844	0.0588	58.5	+ 5.3	760	3525
984	0.0621	63.3	+ 5.6	810	3670
1125	0.0653	70.8	+ 5.8	855	3780
1265	0.0684	77.5	+ 6.0	895	3875

* and ** are shown by points a and b respectively in Fig. 4.

surrounding the discharge. Hence the probability of absorption increases with the increasing concentration of the element"[13]. TWYMAN[14] gives a similar discussion.

It was felt to be of special interest to investigate further this phenomenon, which — so far as we know — has never been referred to yet, by inquiring to what extent changes in flame temperature would upset the equilibrium of the two assumed factors, and thereby cause a shift in points a and b (Fig. 4), if any. Abiding by the manufacturers' advice against using high-temperature gases, such as acetylene, without modification of the instrument, the only alternative left was to try repeating the measurements of potassium interference with the determination of 100 p.p.m. calcium at air-pressures other than the regularly used pressure of 562.5 g/cm^2. However, since any change in air-pressure automatically brings about a corresponding change in aspiration rate of the sprayed solution (Table II), it is clear that there will be two effects. On the one hand it is to be expected that a higher pressure, which allows the consumption of more fuel gas, will raise the flame temperature, while on the other the consequent increase in aspiration rate will tend to lower it. Further investigation of the phenomenon must, therefore, be left to other workers, whose instruments will allow separate control of flame temperature and aspiration rate.

However, it may not be wrong to draw certain tentative conclusions from Table II:

(1) Since increasing the working air-pressure requires the feeding of correspondingly more fuel gas, this seems to result in flames of relatively higher temperatures, as can be seen by comparing the scale readings of the K-free, 100 p.p.m. calcium solution obtained at the same potentiometric setting of the instrument.

(2) The net effect of such an increase in exciting energy on potassium-containing calcium solution seems to be in favour of the above-mentioned effect (a), thus shifting both points a and b in Fig. 4 to the right and raising the maximum positive error.

That the phenomenon may be due to self-absorption of energy within the flame seems to suggest that it is characteristic of the EEL flame source, since such a behaviour has not been reported by other workers using different sources. The EEL flame photometer utilizes a butane–air mixture which passes to a multi-jet burner, where it burns as a broad flat flame. On the other hand, the Lange instrument, for example, uses acetylene, a single jet burner, the resultant flame being long and thin. It is possible that the nature of the EEL flame might give rise to the regions of varying temperatures, at the high potassium concentrations reported here, fulfilling the conditions mentioned above (HARRISON, HARVEY, etc.[11–15]).

Effect of phosphate on calcium

This was studied by spraying a series of 100 p.p.m. calcium solutions containing from 0 to 400 p.p.m. of phosphate prepared from the stock solutions, and calculating the percentage error from the difference between the calcium introduced and the calcium found. Fig. 5 thus obtained in general confirms the results reported by EDGCOMBE AND HEWETT[2] except for two facts:

(a) We obtained the point of inflection at a somewhat higher potassium concentration.

(b) EDGCOMBE AND HEWETT did not point out that the error was *negative*, although it has been shown to be so by many other workers, *e.g.* LEYTON[16] in particular.

It must be mentioned here that this negative error is very considerable, amounting to —92.5% at a concentration as low as 400 p.p.m. of phosphate ion.

Mutual elimination of sodium and phosphate interferences with calcium

COLLINS AND POLKINHORNE[8] and PUFFELES AND NESSIM[17] both refer to the interference effect of phosphate on sodium in the absence of calcium. In order to find out to what extent these two main interfering agents with their opposite effects on calcium, can cancel each other's effects, solutions were prepared from the stock, containing amounts of these ions which were calculated on the basis of Figs. 3 and 5, to cause equal but opposite errors. The results are shown in Table III, indicating almost complete mutual elimination. The small differences observed are probably due to experimental errors.

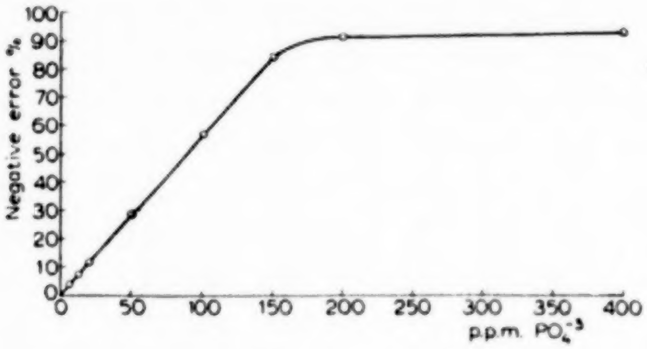

Fig. 5. Effect of PO_4^{-3} on 100 p.p.m. calcium.

TABLE III

MUTUAL ELIMINATION OF SODIUM AND PHOSPHATE INTERFERENCE EFFECTS ON CALCIUM

No.	*Ca^{+2} in soln. p.p.m.*	*PO_4^{-3} in soln. p.p.m.*	*PO_4^{-3} in soln. error %*	*Na^+ in soln. p.p.m.*	*Na^+ in soln. error %*	*Flame photometer scale reading*	*Ca^{+2} found p.p.m.*	*Deviation %*
1	100	0	0	0	0	80.0	100.0	0
2	100	100	—56	3475	+56	79.0	98.8	—1.2
3	100	50	—28	1500	+28	79.5	99.4	—0.6

APPLICATION TO CALCIUM DETERMINATION

(*a*) *Drinking and irrigation water*

Six samples of deep-well and river water were analysed for phosphate, sodium and potassium (Table IV). Calcium was determined by precipitation as oxalate and subsequent titration with permanganate. It is sufficient, for the purpose of this study to report the maximum and minimum results obtained. The water samples first had to be acidified and heated to remove the bicarbonate[4] which is known to have a serious depressing effect on calcium emission. In order to bring the calcium contents within the convenient range of flame-photometric scale reading (0–100 p.p.m. calcium) the water containing the max. amounts of 122 p.p.m. calcium should be diluted (conveniently, 1+1) with demineralized water.

It is obvious that the phosphate and potassium contents of the diluted water samples can cause only a negligible error when sprayed in order to determine calcium. Only the sodium content is significant and would give apparent calcium contents 4.5% higher than the actual ones, according to Fig. 3. A correction of —4.5% would consequently be necessary.

The water sample containing the minimum amount of calcium (34 p.p.m.) requires no dilution before spraying, and in this case the only correction necessary is —1.0% for the positive sodium interference.

It appears possible, therefore, to determine calcium in water directly with the flame photometer, without preliminary separation as oxalate, correcting only for the sodium interference and disregarding the potassium and phosphate errors.

(*b*) *Soil extracts*

Neutral ammonium acetate extracts of six local types of soils were prepared[9], evaporated to dryness and almost all the ammonium acetate sublimed in order to prevent its clogging effect on the capillary atomizer. The residues were then taken up in the minimum amount of 0.1*N* HCl, brought up to a definite volume, sprayed into the flame photometer and the max. and min. values obtained recorded as in the case of water samples (Table IV). The results show that here, too, direct flame-photometric determination is possible, correction only having to be applied for the phosphate contents, since the interferences due to sodium and potassium are negligible.

(*c*) *Plant-ash extracts*

Direct flame-photometric determination was, however, not possible when it came to the ten plant extracts (green and yellow citrus, eucalyptus, desert weed and tobacco leaves), which were found to differ very greatly in their phosphate, sodium and potassium contents (Table IV). The extracts were prepared by ashing about 5 g of the dried plant sample in a silica crucible at 550–600° and extracting the ash with 2.5 ml of conc. HCl and hot water. The extracts were then filtered, cooled and made up to 250 ml with water[18].

TABLE IV

INTERFERENCE ERRORS DUE TO PHOSPHATE, SODIUM AND POTASSIUM IN THE DETERMINATION OF CALCIUM IN WATER, SOIL, PLANTS AND SERUM

	Calcium		*Phosphate*		*Sodium*		*Potassium*	
	range p.p.m.	*dilution required* ×	*sprayed p.p.m.*	*error* %	*sprayed p.p.m.*	*error* %	*sprayed p.p.m.*	*error* %
Water								
Max.	122	2	0.22	0	118	4.5	7.0	0
Min.	34	0	0.15	0	23	1.0	0.8	0
Soil								
Max.	600	6	10	—6	10	0	14	0
Min.	82	0	16	—9	6	0	17	0
Plants								
Max.	1350	14	12	—7	2430	41.5	1643	3.3
Min.	274	3	32	—18	267	8.5	767	4.9
Serum (normal)								
Max.	120	4	35	—20	863	18	60	0.6
Min.	90	4	25	—14	787	16.5	40	0.4

Although it is theoretically possible to calculate the net percentage error in calcium determination resulting from mutual elimination of interference, such a calculation would obviously be impossible unless an analysis is first undertaken to determine sodium, potassium and phosphate. This is not practical when such an analysis is otherwise not required. Clearly the tedious precipitation of calcium seems to be unavoidable in this case, in order to free the calcium from very significant and variable interferences.

(*d*) *Blood serum*

Even though the calcium contents of serum do not necessitate the dilution of 1+3 shown in Table IV, this is advisable because of the inconveniently high viscosity of the serum and the very small volume usually available. It is clear from the analysis of six normal sera (only the max. and min. are given in Table IV) that, in spite of the significant interferences of the individual ions, there is a good chance of mutual elimination, thus leaving only a small positive or negative net percentage error, which, considering the wide range of calcium in normal sera, may be clinically insignificant. It seems justifiable to conclude, therefore, that it appears possible to determine calcium in normal serum for clinical purposes, by spraying its 1+3 dilution directly, without running the risk of a significant error, since normal serum has a more or less stable composition within a certain range. Serum was considered "normal" for this purpose when it complied with the acceptable normal ranges (for adults) of: Na: 315–340, K: 16–22, Ca: 8.5–12 and phosphate 9–14, all in mg %[19].

In Table V a comparison is made of the results obtained by the direct spraying method and those obtained when preliminary precipitation as oxalate is carried out. Serum No. 1 is normal, No. 2 has high phosphate, normal sodium, No. 3 has low phosphate, high sodium, No. 4 has low sodium and phosphate, and No. 5 has high sodium and phosphate.

For normal serum, the agreement between the results of the two methods is good enough. The results of the other sera are influenced by the two main interfering agents: sodium and phosphate, the former tending to raise, and the latter to lower the calcium determined directly. In general, high calcium results are obtained, since the negative error due to phosphate is mostly over-compensated by the positive sodium effect.

It is suggested, therefore, for cases with abnormal serum sodium and phosphate, to be on the safe side and determine calcium by preliminary separation as oxalate, proceeding as follows: remove the supernatant liquid after centrifugation, dissolve the precipitate in 0.05*N* perchloric acid and finally read the solution with the flame photometer.

TABLE V

ANALYSIS OF SERUM SAMPLES

No.	*Sodium p.p.m.*	*Phosphate p.p.m.*	*Calcium p.p.m.*		
			By precipitation as oxalate	*By direct spraying*	*Difference %*
1	3300	100	110	112	+ 1.8
2	3250	140	105	102	— 2.8
3	3600	90	115	123	+ 7.0
4	3100	70	95	100	+ 5.3
5	3650	80	120	129	+ 7.0

SUMMARY

An investigation of the possibilities for the direct determination of calcium with a single-cell filter flame photometer, without preliminary separation as oxalate, led to the following conclusions:

Calibration curves for 100 p.p.m. of calcium are rectilinear.

Sodium causes an appreciable positive error.

The error due to potassium interference is relatively much smaller than that due to sodium. Up to a certain concentration it is positive and increases with the concentration, then the emission seems to be gradually depressed and the error finally becomes negative.

Phosphates cause a very significant negative error, which tends to be asymptotic. The "radiation buffer" method of correction is not practical here because the max. error is too high (—92.5%).

Except for extreme cases, calcium can be determined by direct spraying, without preliminary separation as oxalate:

(a) in drinking and irrigation water, correction being necessary only for sodium interference,

(b) in soil extracts, correcting only for phosphate effects,

(c) in normal blood sera, without clinically significant corrections at 1 + 3 dilution.

Owing to the large variations in the contents of Na, K and PO_4^{-3} in plants, calcium cannot be determined in plant-ash extracts without preliminary separation as oxalate. This applies also to abnormal sera, although there the variations in Na and PO_4^{-3} content are not so large.

RÉSUMÉ

Les auteurs ont examiné les possibilités d'un dosage direct du calcium dans des extraits de plantes et de sol, dans l'eau et dans le sérum, par photométrie de flamme, sans séparation préliminaire comme oxalate.

ZUSAMMENFASSUNG

Es wird die Möglichkeit untersucht, Calcium direkt in Pflanzen- oder Bodenextrakten, in Wasser oder Serum flammenphotometrisch zu bestimmen ohne vorherige Isolierung als Calciumoxalat.

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SPECTROPHOTOMETRIC DETERMINATION OF PYRIDOXAL-5-PHOSPHATE

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The existing enzymic method for the determination of pyridoxal-5-phosphate (Py5P), which is based on the activation of tyrosine apodecarboxylase[1], is highly specific for Py5P, but cumbersome and time-consuming. On the other hand, the existing colorimetric and spectrophotometric methods[1,2], though comparatively rapid and simple, are to a large extent unspecific.

The present paper describes a new and simple procedure for a spectrophotometric determination of Py5P, based on the optical properties of the reaction product which is formed when Py5P reacts with cyanide. The reaction itself, which has been described by us only recently[3], has been studied further and the results are also included in the present paper.

EXPERIMENTAL

Reagents

0.2*M* sodium phosphate buffer, pH 7.4.

0.03*M* potassium cyanide, in 0.2*M* sodium phosphate buffer, pH 7.4.

0.0001*M* solution of pyridoxal-5-phosphate (Hoffmann-La Roche, Switzerland), in 0.2*M* sodium phosphate buffer. This standard solution must be prepared just before use from a 0.001*M* stock solution, which should be kept frozen when not in use.

Procedure

The solution to be examined is diluted so that it contains not more than 25 μg Py5P/1 ml, and the pH is adjusted to 7.4. From this solution two 3 ml portions are taken, *A* and *B*. To the first, *A*, 0.1 ml of KCN is added and to the second, *B*, 0.1 ml sodium phosphate buffer. After incubation for 45 min at 50°, the optical density is measured at 385 mμ in a Beckman spectrophotometer model DU. The difference in optical density between *B* and *A* is compared with a calibration curve obtained with a range of Py5P standards.

RESULTS

Absorption spectra

When Py5P reacts with KCN in 0.2*M* sodium phosphate buffer, pH 7.4, profound changes in the ultraviolet absorption spectrum of the former occur, as shown in Fig. 1. The characteristic absorption maximum at 385 mμ is completely levelled off, while the maximum at 320 mμ is intensified, with a slight shift towards shorter wavelengths. A relationship exists between the spectral modifications and the amounts of KCN added, up to the molar ratio of 1 : 1 (Fig. 2), showing that the reaction between Py5P and KCN can be considered complete when the reactants are present in equimolecular concentrations. The complete disappearance of the 385 mμ maximum is probably due to the formation of an addition compound, namely a cyanohydrin, since this maximum is associated with the aldehyde group at C_4, which is the only one capable of reacting with cyanide. Completeness of the reaction is secured by the addition of excess KCN.

Paper electrophoresis

A further indication of the formation of an addition compound between Py5P and KCN is provided by the results illustrated in Fig. 3, which shows the difference of the mobilities between Py5P and its reaction product with cyanide.

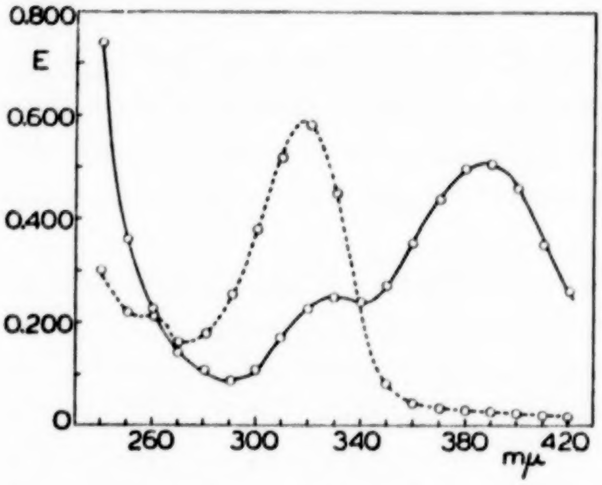


Fig. 1. Absorption spectra: Py5P, $10^{-4}M$, (solid line) and the same after addition of KCN (broken line) (see text).

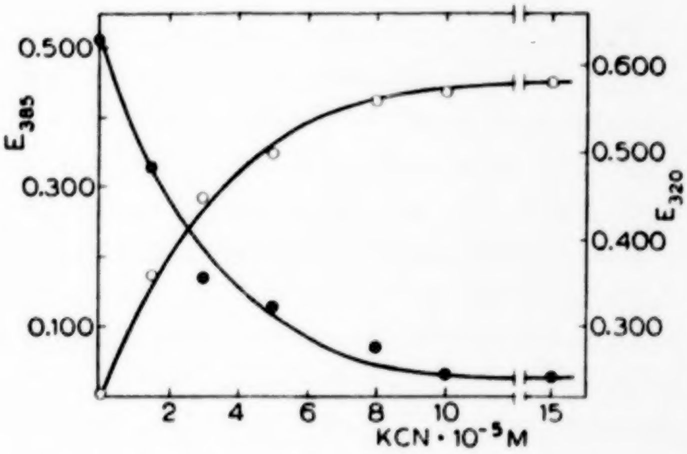


Fig. 2. Optical density changes at 320 mμ (o—o) and at 385 mμ (●—●) as a function of KCN concentration.

Influence of pH

The reaction between Py5P and KCN, as can be expected, is influenced by the hydrogen ion concentration. The rate of formation of the addition compound (cyanohydrin) at different pH values is illustrated in Fig. 4. The optimal pH appears to be near neutrality, on the alkaline side, where Py5P still has the structural formula (I)

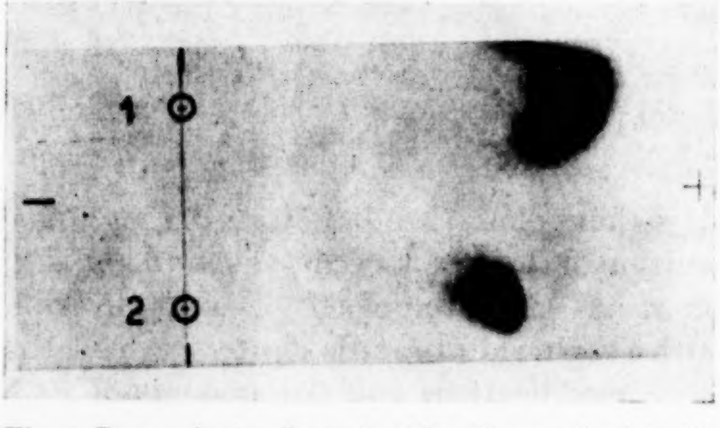


Fig. 3. Paper electrophoresis of Py5P cyanohydrin (1) and of Py5P (2). Experimental conditions according to SILIPRANDI, SILIPRANDI AND LIS[5].

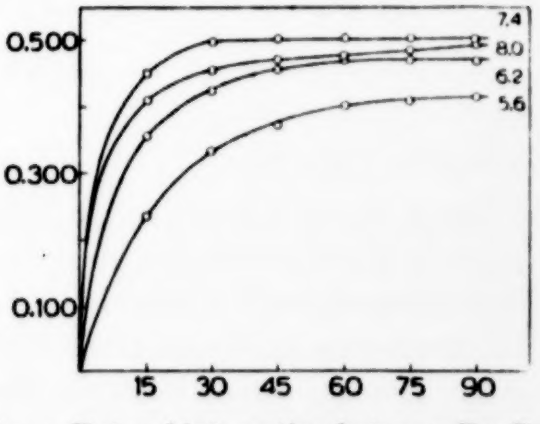
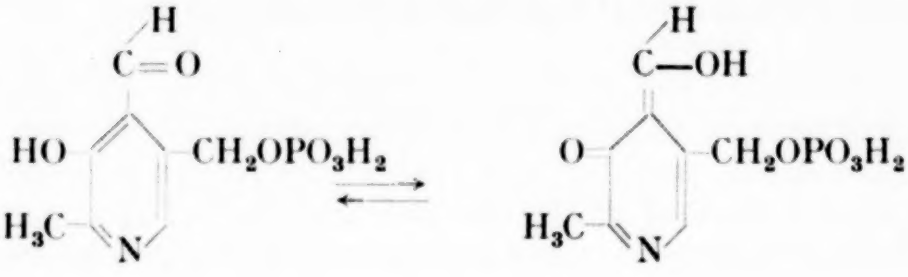


Fig. 4. Rate of interaction between Py5P and KCN at different pH values. Ordinate: decrease of the optical density at 385 mμ; abscissa: time in minutes.

References p. 50

which favours the interaction with KCN, and where KCN is not hydrolysed. At pH 9.0, Py5P does not react with KCN because structure (II) prevails[4].



(I) (II)

Linearity of the reaction

The optical density decrease at 385 mμ in the presence of a large excess of KCN is proportional to the concentration of Py5P present over a range of 0–25 μg, as shown in Fig. 5. The optical density increase at 320 mμ is also proportional to the concentration, but it has not been chosen to measure Py5P because almost every B_6 member has its characteristic maximum at this wavelength.

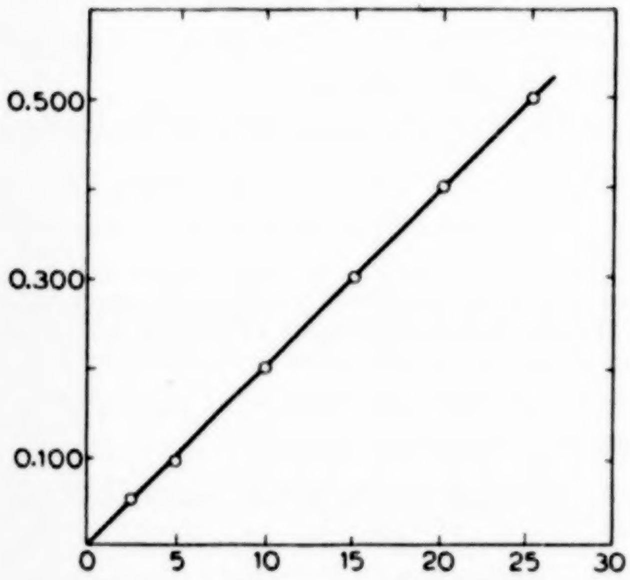


Fig. 5. Calibration curve. Abscissa: μg Py5P/1 ml; ordinate: decrease of the optical density at 385 mμ.

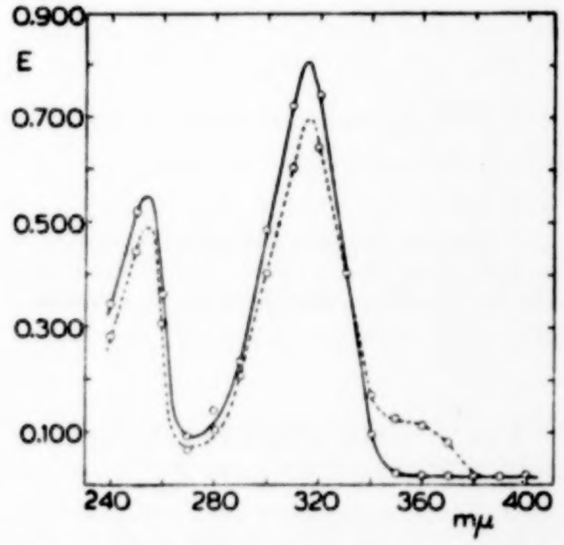


Fig. 6. Absorption spectra: pyridoxal hydrochloride, $10^{-4}M$ (solid line), and the same after addition of KCN (broken line).

Specificity of the reaction

The following structural analogues, belonging to the B_6 group, have been examined in order to test the specificity of the reaction with KCN and the possible interferences: pyridoxal hydrochloride (Bios Lab., U.S.A.), pyridoxine dihydrochloride (Italfarmaco, Italy), pyridoxamine phosphate (S.I.T.I., Italy), pyridoxal hydrochloride ethylacetal and pyridoxamine hydrochloride (Hoffmann-LaRoche, Switzerland). No changes appeared in the absorption spectra of the above-listed substances following the addition of KCN, except for pyridoxal hydrochloride, the spectrum of which is reported in Fig. 6. As can be seen, the addition of KCN produces an increase of the optical density in the region from 330 to 380 mμ, with a maximum at 360 mμ. At 385 mμ there is a very slight increase which can be neglected in practice.

DISCUSSION

The spectrophotometric procedure that has been described is very specific for Py5P and in this respect it is equalled only by the enzymic method of GUNSALUS AND SMITH[1]. The enzymic method, however, as pointed out already in the INTRODUCTION, is rather cumbersome and tedious, and is not suitable for occasional assays, such as those required to determine the purity of a Py5P preparation or the Py5P yield in artificial as well as in biological syntheses.

The colorimetric methods, on the other hand, are not specific unless a previous separation, chromatographic or electrophoretic, is made, but this eliminates the advantage offered by the simplicity and rapidity of the colorimetric methods themselves.

The spectrophotometric method suggested by SCHOTT AND CLARK[6], which is based on the decrease of optical density at 375 mμ and the increase at 327 mμ, following the addition of *m*-hydroxypropadrine, does not seem reliable.

The sensitivity of the present method, based on a spectral peculiarity of Py5P in presence of KCN, is comparable with that of colorimetric and spectrophotometric methods, but inferior to that of enzymic assay. The extreme simplicity both of reagents and procedure and the high specificity represent its main features.

We are studying the possible application of the present procedure to biological materials.

SUMMARY

A simple and specific spectrophotometric procedure for the estimation of pyridoxal-5-phosphate is described, based on the complete disappearance of the absorption maximum at 385 mμ following the incubation with potassium cyanide.

RÉSUMÉ

Une méthode simple et spécifique est proposée pour le dosage du pyridoxal-5-phosphate, par spectrophotométrie.

ZUSAMMENFASSUNG

Es wird eine einfache, spezifische spektrophotometrische Methode zur Bestimmung von Pyridoxal-5-phosphat beschrieben.

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MERCURY CHLORIDE FILM ANODE

I. STUDY OF THE CHARACTERISTICS OF A MERCURY CHLORIDE FILM ANODE BY CHRONOPOTENTIOMETRIC METHODS

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INTRODUCTION

The most common electrode materials for anodic oxidation are platinum, gold, or graphite. Reproducible results are obtained at these electrodes if they are either chemically or mechanically pre-treated prior to each run.

The mercury electrode is widely used for reductions due to its high hydrogen overvoltage and reproducible surface. It is severely limited as a practical working anode by the dissolution of mercury itself at low anode potentials.

Several workers have observed[1-3] that some unusual phenomena occur at the mercury surface when it is polarized anodically in the presence of halide solutions. The so-called anodic passivation of mercury in chloride media has been extensively studied[4-6] by constant current methods.

A similar effect has been observed in this laboratory where the passivation is characterized by a well defined potential rise to values of 1 V or more. This passivation is due to the formation of a film of mercury chloride that effectively limits the continued mercury oxidation. Such a Mercury Chloride Film Anode (MCFA) may be used for the oxidation of substances in the bulk of the solution. As reported earlier[7] several substances have been successfully oxidized using both conventional voltage-scan and chronopotentiometric techniques at a quiet MCFA.

In this paper the characteristics of the MCFA obtained through chronopotentiometric studies are discussed in detail. The MCFA is evaluated as an analytical tool and compared to the platinum electrode. The results obtained by the voltage-scan method will be reported in a separate paper.

EXPERIMENTAL

The chronopotentiometric equipment and circuit were conventional in all respects. Two electrolysis cells were constructed following the design illustrated by REILLEY, EVERETT AND JOHNS[8]. The lower and upper Lucite plugs (o.d. 50 mm) were machined and bevelled on a lathe to fit tightly a 50 mm length of pyrex tubing (i.d. 45 mm). One-quarter inch cavities were machined for the mercury pools in the lower plugs. The pool areas were calibrated through cadmium ion reductions[8] and found to be 1.47 and 1.60 cm^2. Because Lucite is not wetted by the solution or mercury, the interface is reproducible and constant. Contact with the mercury pool was made by a platinum wire which was inserted through a small hole in the bottom of the cavity and sealed with polystyrene. Polystyrene also served as a sealing agent between the lower plug and the pyrex tubing. The upper plug of Lucite had 4 holes drilled for inserting 2 saturated calomel electrodes (S.C.E.), a bubbling tube terminating in a sintered disk, and a nitrogen outflow. The saturated calomel electrodes were of the design described earlier[9]. The upper plug was permanently clamped to a supporting stand. The cell could be then inserted easily from the bottom and held into position with 2 rubber bands connected to small metal hooks drilled into the sides of the Lucite plugs.

Reagent-grade inorganic chemicals and Fisher triple-distilled instrument-grade mercury were used throughout the work without further purification. Stock solutions $2M$ in potassium chloride with pH adjusted to *ca.* 2.5 with hydrochloric acid were prepared fresh every three days. Erratic results were obtained with old potassium chloride solution which was probably due to formation of surface-active substances by bacterial growth.

Stock solutions of the organic substance to be oxidized in $0.01\,M$ concentration were prepared anew before each series of experiments. Appropriate amounts of stock organic solution and $2M$ potassium chloride were mixed to give final solutions for chronopotentiometry which were $0.2M$ in potassium chloride and about 10^{-3} to $10^{-4}M$ in organic constituent.

PROCEDURE

Approximately 0.5 ml of mercury was delivered from a 10-ml buret into the cavity of the cell. The sample solution with pH adjusted to *ca.* 2.5 was added to the cell. The solution was deaerated for 5 min to remove any dissolved oxygen. Oxygen reacts with mercury in the acidic chloride medium to form mercurous chloride, and more reproducible results are obtained after removal of oxygen. After deaeration the solution was allowed to quiet for *ca.* 1 min and then constant current of desired level was switched on for the chronopotentiogram.

FILM FORMATION

The theory of chronopotentiometry has been well established by the work of GIERST AND JULIARD[10], DELAHAY[11] and others.

Fig. 1, A shows the experimental potential–time pattern (chronopotentiogram) for the anodic polarization of a supporting electrolyte solution, $0.20M$ in potassium chloride and *ca.* $0.002M$ in hydrochloric acid (pH 2.7). A constant current of $240\,\mu A/cm^2$ was initiated at the point, $t = 0$, and the resulting chronopotentiogram displays four small potential hold-ups. The anodic potential of $+1.4$ V *vs.* S.C.E. is reached in less than 20 sec.

Fig. 1, B shows the chronopotentiogram of a $2 \cdot 10^{-3}M$ solution of N,N-dimethyl-*p*-phenylenediamine (DPP) in the same supporting electrolyte as that used for the

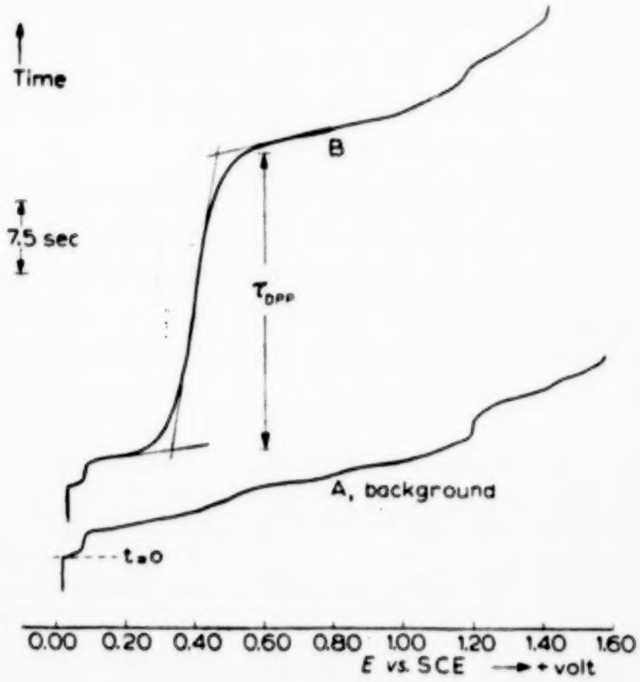

Fig. 1. Potential–time patterns.
A. Background, anodic polarization of mercury pool in $0.2M$ potassium chloride solution.
B. Oxidation of N,N-dimethyl-*p*-phenylenediamine (DPP).

chronopotentiogram of Fig. 1, A. The first wave is for formation of the mercurous chloride film followed by a clearly defined wave for the oxidation of DPP.

This phenomenon has not been observed previously in polarographic work at the dropping mercury electrode (D.M.E.) since the expanding mercury surface and the time interval between successive drops do not favor complete film formation. This is in agreement with the work of KOLTHOFF AND MILLER[12] who found from studies of current-voltage curves at the D.M.E. in the presence of chloride ion, that the diffusion current when corrected for residual current was proportional to the chloride concentration between $2 \cdot 10^{-3}$ and $10^{-5}M$. At higher chloride concentrations the C-V waves had an abnormal appearance which was caused by a film of calomel around the mercury drop.

A. Chloride concentration and current density

In Fig. 2 chronopotentiograms at a constant current of 167 μA/cm² are shown for potassium chloride concentrations varying from 0.04 to 0.90M in 0.002N hydrochloric acid. The initial wave is the formation of mercurous chloride that proceeds until the electrode becomes "passive". By the term "passive" it is meant that the electrode has become coated with a film of mercurous chloride. The filmed electrode, as will be discussed later, will now sustain oxidations of substances in the bulk of the solution, *i.e.*, it substantially operates as an inert working anode. This is seen in Fig. 1, B, where, following the small film wave, there is observed a typical chronopotentiogram for the oxidation of N,N-dimethyl-*p*-phenylenediamine (DPP).

The passivation time, T_1, refers to the first potential hold-up or wave. The time

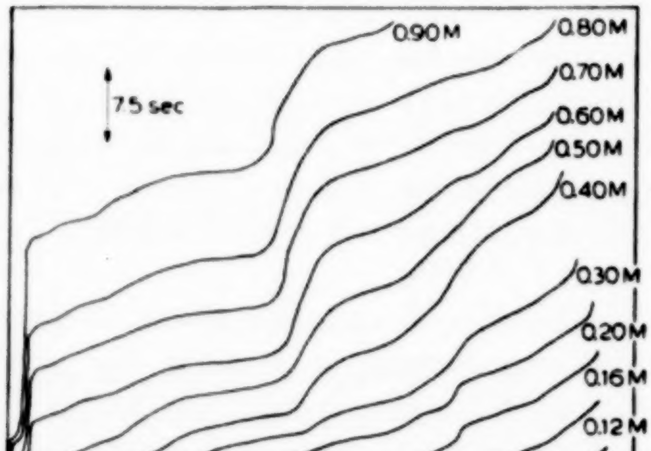

Fig. 2. Anodic potential-time patterns for varying potassium chloride concentrations.

required to deplete the chloride ion concentration at the electrode surface (in the usual sense of chronopotentiometry) is at least a factor of 100 times the value of T_1 observed experimentally.

The $E_{1/4}$ of the first wave follows closely the relationship

$$E_{1/4} = E^\circ - 0.0591 \log \frac{(\mathrm{Cl}^-)}{2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

Where E° is the standard potential *vs.* S.C.E. for the reaction:

$$2\mathrm{Hg} + 2\mathrm{Cl}^- = \mathrm{Hg_2Cl_2} + 2e^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

The experimentally determined $E_{1/4}$'s are in good agreement with the calculated values with less than 10 mV deviation. The $E_{1/4}$ corresponding to the point $t = \tau/4$ on the first wave assumes that it is similar to the polarographic $E_{1/2}$. As pointed out by DELAHAY AND BERZINS[13] the potential $E_{1/4}$ corresponding to $t = \tau/4$ has no particular significance in cases of an irreversible wave.

The plot of the variation of $E_{1/4}$ with the log of $^1/_2$ chloride concentration in the bulk of the solution gives a slope of 0.064 in reasonable agreement with the theoretical value of 0.059. These data leave little doubt that the first wave corresponds to the formation of mercurous chloride.

From the chronopotentiogram of the 0.20M potassium chloride solution, two significant potential hold-ups may be seen above +0.30 V *vs.* S.C.E. At higher chloride concentrations, the T_1 increases followed by only one major potential hold-up prior to about +1.4 V *vs.* S.C.E. The $E_{1/4}$'s of all the waves are dependent on the chloride concentration which suggests not only further oxidation of mercurous chloride to mercuric chloride, but also oxidations involving mercury chloride complex ions. No systematic study has been made to determine the exact nature of these potential hold-ups.

In this paper further discussion of the background film waves will be devoted to the first and second potential hold-ups since they have the largest transition times and occur in the range of most interest for analytical purposes. They occur at *ca.* +0.080 and +0.55 V *vs.* S.C.E. for a solution 0.2M in KCl. The time for the second wave will be referred to henceforth as T_2.

T_1 and T_2 vary with the chloride concentration and the current density. The variation of $(T_1)^{1/2}$ with the chloride concentration is shown in Fig. 3. The pH of the solution was adjusted to *ca.* 2.7 with HCl. The constant current used was 167 μA/cm². The minimum of the curve is between 0.2 to 0.4M chloride. At lower than approximately $5 \cdot 10^{-3}M$ chloride the T_1 decreases due to the depletion of chloride at the surface of the mercury before film formation is complete. Therefore, in this region, $(T_1)^{1/2}$ changes linearly with the bulk chloride concentration as in the usual diffusion controlled chronopotentiograms.

The experimental variation of T_1 with current density follows the relationship:

$$i_0 T_1^K = 2.7 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

where i_0 is the current density in μA/cm², T_1 is the time in seconds. This equation can be used, if desired, to predict T_1 for any current density. The value of K found for 0.2M potassium chloride solutions at pH 2.5 was 0.60.

The variation of T_2 with current density and chloride concentration has been determined. The optimum conditions for analytical purposes are those which give minimum values of T_1 and T_2. These conditions are current densities between 100 and 400 μA/cm^2 and chloride concentrations of 0.2 to 0.3M.

B. Presence of other ions

Anions which form very stable complexes or salts with mercurous ion such as oxalate, sulfate, phosphate, and iodide ions can be tolerated in the 0.2M potassium chloride background solution only up to about 0.05M levels. Phosphate ion alone in the solution forms a film with mercury similar in behavior to chloride. The phosphate film is not satisfactory for analytical applications.

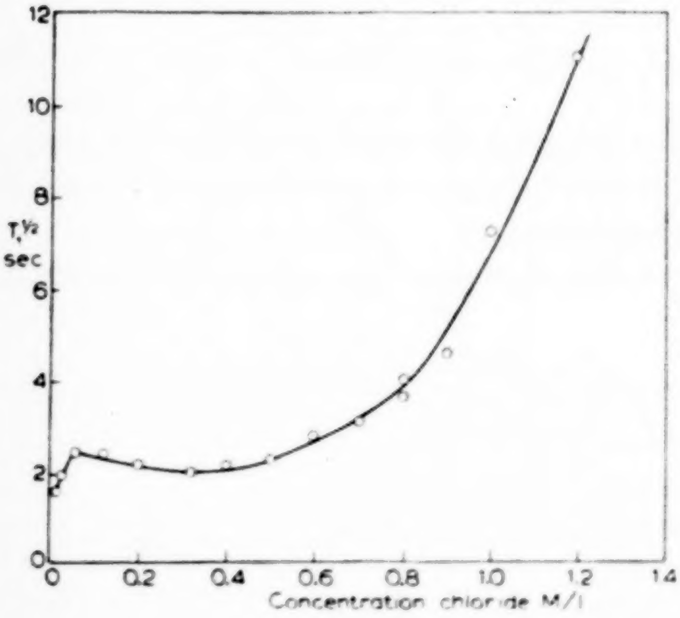

Fig. 3. Square root of passivation time, $T_1^{1/2}$, *vs.* chloride concentration.

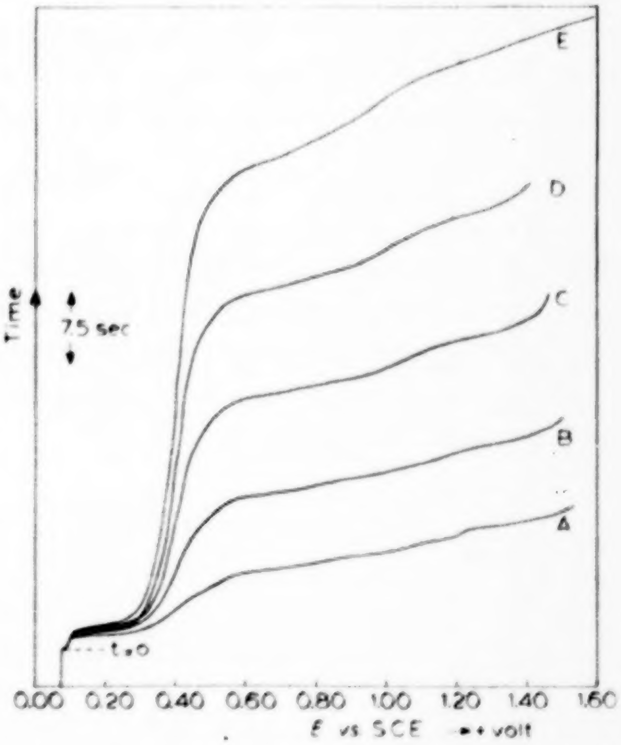

Fig. 4. Chronopotentiograms for oxidation of DPP. A to E, 1.0 to 5.0·10^{-3}M solutions, respectively.

Indifferent anions, such as nitrate, acetate, fluoride, and perchlorate which do not form strong complexes may be tolerated to a concentration of *ca.* 0.10M. Higher concentrations of these anions weakens the film apparently due to incorporation in the film lattice. Their deleterious effect is obvious on the chronopotentiograms by the appearance of several sharp, saw-toothed patterns. These appear as the normally invisible film is ruptured. Small fissures and cracks are then visible on the surface of the electrode.

In basic solutions the background waves become erratic due to competition for formation of the oxide which also disrupts the film. The potential of the electrode under these conditions will remain constant at *ca.* +0.57 V *vs.* S.C.E. As the electrolysis continues, a mixture of a yellow and white precipitate is observed on the surface of the electrode. The precipitate is probably a mixture of mercuric oxide and mercury chloride.

C. Vibrations

Sharp vibrations tend to rupture the film. Small blips are observed on the chronopotentiograms. Vibrations were eliminated by placing the cell stand on a 4-inch thick piece of polyurethane padding.

ANALYTICAL APPLICATIONS

Oxidation of DPP

Fig. 4 shows chronopotentiograms for DPP in the background medium of $0.20M$ potassium chloride and $0.002N$ hydrochloric acid (hereafter called background electrolyte). The current density used in the electrolysis was 420 μA/cm². The concentrations of DPP were 1.0, 2.0, 3.0, 4.0 and $5.0 \cdot 10^{-3}M$ for Figs. 4, A to 4, E, respectively. A well defined oxidation wave is observed for all these concentrations. A plot of the square root of the transition time, $\tau_{\mathrm{DPP}}^{1/2}$, with concentration of DPP gives excellent linearity. The transition time, τ_{DPP}, is given by:

$$\tau_{\mathrm{DPP}}^{1/2} = \frac{\pi^{1/2} n F C^b D^{1/2}}{2 i_o} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

where n is the number of electrons involved in the electrode reaction; F is the Faraday; C^b is the bulk concentration of the electroactive species; i_o the current density; and D the diffusion coefficient of the electroactive species.

If the electrode reaction involves consecutive processes[13], the transition times τ_1 and τ_2 would be given by:

$$(\tau_1 + \tau_2)^{1/2} - \tau_1^{1/2} = \frac{\pi^{1/2} n_2 F D_2^{1/2} C_2^b}{2 i_o} \qquad (5)$$

TABLE I

OXIDATION OF DPP AT MCFA AND Pt ELECTRODES

Conc. DPP $\times 10^3$	*Conc.* KNO_3	T_1 *(sec)*	τ_{DPP} *(sec)*	$E_{1/4}$ *(V vs. S.C.E.)*
A. MCFA: (i_o = 205 μA/cm², background solution $0.20M$ KCl, pH = 3.2)				
2.5	0	9.37	59.2	0.340
2.5	0.005	14.2	57.0	0.340
2.5	0.010	13.9	62.0	0.340
2.5	0.05	7.50	63.0	0.338
2.5	0.10	8.25	60.0	0.335
2.5	0	7.50	60.0	0.340
			Average 60.2 ± 1.5	0.339 ± 0.002
			Average deviation 2.5%	0.6%
B. Pt electrode: (i_o = 245 μA/cm², background solution $0.20M$ KCl, pH = 3.2)				
2.5	0		34.1	0.334
2.5	0.005		32.3	0.340
2.5	0.010		33.0	0.342
2.5	0.050		33.0	0.350
2.5	0.10		33.5	0.350
2.5	0		31.1	0.341
			Average 32.8 ± 0.8	0.343 ± 0.005
			Average deviation 2.4%	1.5%

where n_2 is the number of electrons involved in the electrode reaction for the second substance; D_2, the diffusion coefficient for the second substance; and C_2^b, the bulk concentration of the second substance. If this were true in the present case under consideration, $[(\tau_1 + \tau_2)^{1/2} - \tau_1^{1/2}]$ would be proportional to the concentration of DPP, where τ_1 and τ_2 refer to the transition time for the film formation and oxidation of DPP, respectively.

The data of Table I clearly show that τ_{DPP}, within experimental error, is independent of the variation of the transition time for film formation. This indicates that the oxidation of DPP proceeds independent of the film reaction. Table I also includes comparison data for the chronopotentiometric oxidation of DPP at a platinum foil electrode.

The calibration curves A, B and C for DPP in Fig. 5 are for current densities of 420, 240, and 167 μA/cm², respectively. The product $i_0\tau^{1/2}/C^b$ was not constant. The variation was less than 20% for these current levels. In a purely diffusion-controlled reaction with no complications, $i_0\tau^{1/2}/C^b$ is a constant.

The plots of log $\dfrac{\tau^{1/2} - t^{1/2}}{t^{1/2}}$ *vs.* potential of DPP at both types of electrodes show close similarity with a "break" appearing in the curve at *ca.* +0.38V *vs.* S.C.E. (Fig. 6). The DPP concentration is $2 \cdot 10^{-3} M$, current 167 μA/cm². The pH's of the solutions are 4.0 and 3.88 for the MCFA and Pt electrodes, respectively. The slopes of the curves for the MCFA are 0.135 and 0.064, and for the Pt electrode, 0.088 and 0.070. The reason for the "break" in the curve is not known although curves for such plots have been observed in instances of irreversible electrode reactions at the DME[14]. The similarities

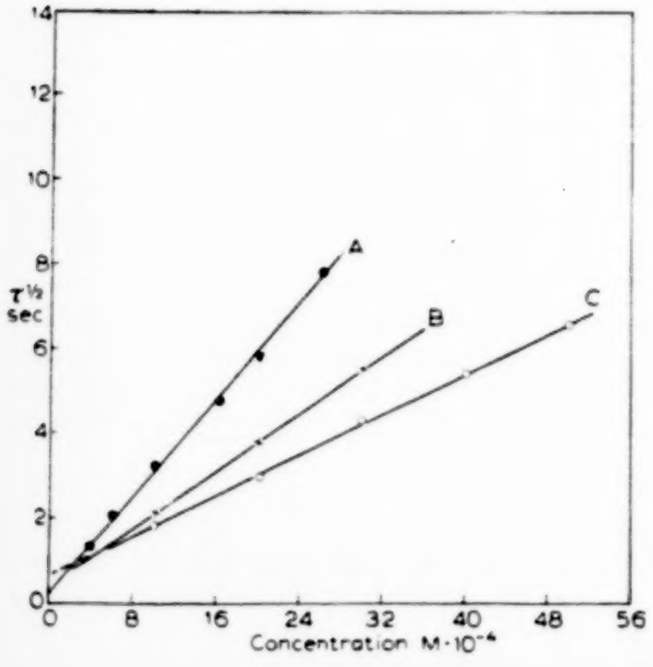

Fig. 5. Calibration curves for DPP oxidation at varying current densities. A. 420 μA/cm²; B. 240 μA/cm²; C. 167 μA/cm².

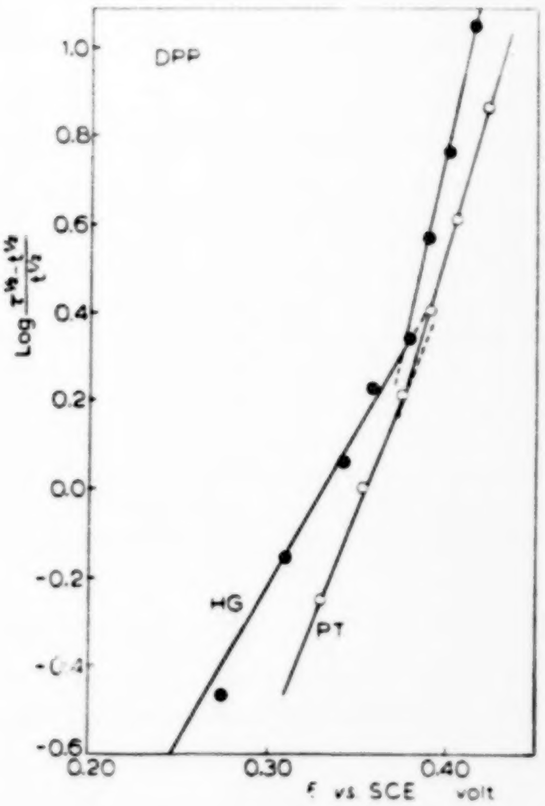

Fig. 6. Plot of log $\dfrac{\tau^{1/2} - t^{1/2}}{t^{1/2}}$ *vs.* electrode potential for oxidation of DPP at platinum and MCFA electrodes.

between the Pt electrode and MCFA for the oxidation of DPP suggests that the film on the surface of the mercury is functioning essentially as an "inert" electrode.

Oxidation of other compounds

The various organic molecules listed in Table II can be oxidized at the MCFA. In all cases except that of hydroquinone, the $E_{1/4}$'s at platinum and MCFA electrodes are in close agreement. Calibration curves for aniline, hydroquinone and 3,3'-dimethylbenzidine (*o*-tolidine) at a constant current level of 240 μA/cm^2 are shown in Fig. 7. The sensitivity for aniline is low. Linear calibration curves may be obtained for the other compounds with the exception of *o*-phenylenediamine and 8-amino-1,3,6-naphthalenetrisulfonic acid (Koch's Acid). Anomalous behavior is observed for *o*-phenylenediamine above a concentration of about $2.5 \cdot 10^{-3} M$ where the $\tau^{1/2}$ decreases markedly in the calibration plot. The reason for this behavior is not known.

TABLE II

COMPARISON OF OXIDATIONS AT PLATINUM AND MCFA

Compound	*pH*	*$E_{1/4}$ (Pt)* *V vs. S.C.E.*	*$E_{1/4}$ (MCFA)* *V vs. S.C.E.*
DPP	2.7	0.41	0.37
	4.3	0.33	0.33
Aniline	3.5	0.81	0.82
o-Phenylenediamine	4.0	0.38	0.43
p-Phenylenediamine	3.2	0.37	0.5
Hydroquinone	2.7	0.42	0.95
Ferrocyanide	2.7	0.40	—
1,10-*o*-Phenanthroline ferrous	3.5	1.10	0.96
8-Amino-1,3,6-naphthalenetrisulfonic acid (Koch's Acid)	3.1	0.76	0.80

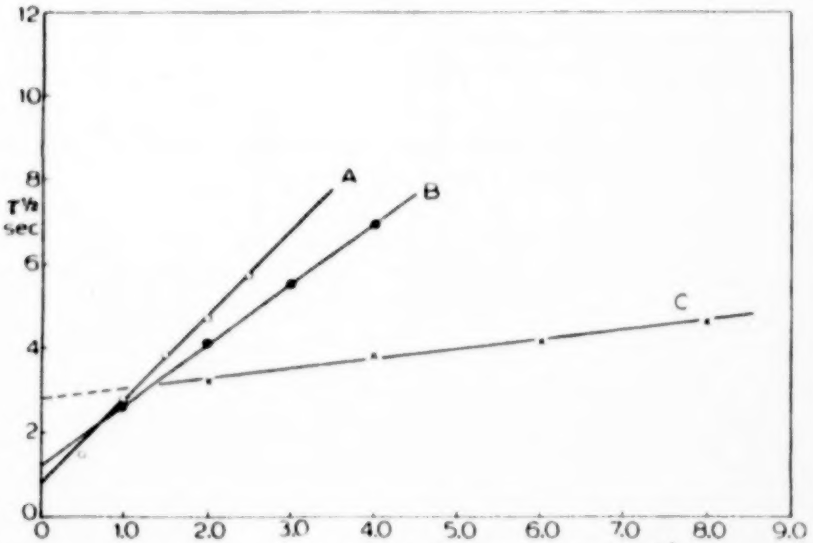

Fig. 7. Calibration curves. A. 3,3'-Dimethylbenzidine (*o*-tolidine). B. Hydroquinone. C. Aniline.

For Koch's Acid, a similar effect is found above a concentration of *ca.* $2 \cdot 10^{-3} M$.

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In this case, the reason for the decrease in transition time is believed to be related to the surface-active nature of Koch's Acid. The strong absorption on the surface of mercury greatly enhances the passivation time, T_1, and consequently, the thickness of the film formed. The thick film hinders the oxidation of Koch's Acid and τ then decreases. Other surface-active agents such as gelatin, produce the same deleterious effect. Solid calomel has been observed frequently on the anode surface under these conditions.

Inorganic ions, such as Fe(II), U(IV), Co(II), ferrocyanide, bromide and iodide, do not exhibit oxidation at the MCFA. The last three ions interfere with the mercury chloride film formation due to competitive formation of insoluble mercury salts. T_1 is then large and solid precipitate is often observed on the electrode surface.

Re-use of MCFA

A possible advantage of this new electrode system is that it requires no special cleaning or pre-treatment procedures. After an oxidation run, the surface may be readily cleaned by cathodic stripping. Preliminary experiments indicate that successive determinations may be performed with the same mercury pool, using cathodic stripping to renew the electrode surface. A reproducibility of $\pm 3\%$ for 5 successive determinations of DPP has been obtained in this fashion.

ACKNOWLEDGEMENTS

We wish to express our appreciation to the Research Corporation of America for a grant in partial support of this work. Samples of Koch's Acid were kindly supplied by E. I. du Pont de Nemours and Company. The assistance of MARTHA KELLY in preparing the manuscript is gratefully acknowledged.

SUMMARY

The Mercury Chloride Film Anode (MCFA) is proposed as a new working anode which compares favorably with platinum or other inert metal electrodes.

Only organic compounds have been oxidized thus far at the MCFA. Since the oxidation of organic molecules is of considerable interest this is not a serious limitation. The use of this electrode is restricted to pH's less than 5. This, coupled with the interferences of high concentrations of certain anions like iodide, phosphate, and sulfate, represent the most serious restrictions to MCFA's analytical usage. A further interesting possibility of this electrode is its use as a working cathode or anode in solutions containing both reducible and oxidizable species.

RÉSUMÉ

L'anode à film de chlorure de mercure est proposée; elle peut être comparée avantageusement à l'électrode de platine ou à d'autres électrodes de métal inerte. D'autre part, elle peut fonctionner soit comme cathode, soit comme anode dans des solutions renfermant des substances oxydables ou réductrices.

ZUSAMMENFASSUNG

Es werden die Vorteile der „Quecksilberchloridfilm-Anode" gegenüber der Platinelektrode oder solchen aus anderen inerten Metallen beschrieben. Sie kann in Lösungen, die reduzierbare oder oxydierbare Substanzen enthalten, sowohl als Kathode wie auch als Anode verwendet werden.

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MERCURY CHLORIDE FILM ANODE

II. INVESTIGATION OF THE CHARACTERISTICS OF THE MERCURY CHLORIDE FILM ANODE BY VOLTAGE-SCAN METHOD

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INTRODUCTION

An investigation of the anodic passivation phenomenon at the mercury pool electrode in the presence of chloride ion has led to the development of a Mercury Chloride Film Anode (MCFA). Its characteristics as applied to the oxidation of substances by the chronopotentiometric method were reported earlier[1].

In chronopotentiometry the film was formed in the presence of the substance to be oxidized in the background potassium chloride solution. This led to difficulties of non-reproducibility or no passivation in cases where the substance to be oxidized formed very stable salts with mercurous ion, or was strongly absorbed on the mercury surface. This difficulty may be eliminated by forming the film by voltage-scan prior to the introduction of the oxidizable substance.

The objectives of this paper were to evaluate the characteristics of the MCFA as a working anode for the oxidation of substances by the voltage-scan method. As a useful analytical tool, a method of reproducibly forming the film and applying it to oxidations will be discussed. The variation of peak current with concentration, sensitivity, and half-peak potentials obtained will be compared with the previously reported chronopotentiometry work.

APPARATUS AND REAGENTS

A Lucite cell described previously[1] was used throughout this work. The area of the mercury pool was $1.60\ cm^2$.

The polarizing unit was a 50-ohm $\pm$ 0.5% linearity 10-turn Helipot. It was connected to a speed changer (Metron Instrument Co., Denver, Colo.) driven by a reversible, synchronous motor. By appropriate adjustment of the speed changer, scan rates from 200 to 5000 mV/min were possible. The polarizing voltage was obtained from four $1\text{-}\frac{1}{2}$ V dry cells, connected in such a manner, that a voltage range from -3 to $+3$ V could be scanned.

The currents were determined by measuring the voltage drop across a calibrated decade resistance box in series with the circuit using a Varian recorder (10 mV full scale deflection). No damping was applied and the pen movement was limited only by the natural period of the recorder (1 second full scale). The chart speed of the recorder was 2 in./min.

The electrode potential *versus* an auxiliary saturated calomel reference electrode (S.C.E.) was also monitored by a Leeds and Northrup model 7664 pH meter which fed into a Leeds and Northrup Speedomax recorder adjusted for a 2.0-V full scale deflection. This system was used when it was desired to compare the applied voltage to the actual potential of the electrode. The L and N recorder operated at a chart speed of 2 in./min.

Bethlehem Apparatus Company instrument mercury was used without further purification.

Stock solution of 0.20*M* potassium chloride with pH adjusted by hydrochloric acid to about 2.5 (background electrolyte) was prepared fresh every 3 days for reasons previously described[1]. The 0.01*M* stock solutions of oxidizable substances were prepared containing 0.20*M* potassium chloride and pH adjusted to *ca.* 2.5 (hydrochloric acid or sodium hydroxide). They were prepared prior to each series of runs.

PROCEDURE

Approximately 0.5 ml of mercury was delivered to the cavity of the Lucite cell by a 5.0-ml buret. Care must be taken against stopcock grease or other contaminants coming in contact with the mercury. To the cell was added 30 ml of the background electrolyte. The cell was placed in position and the solution deaerated for ca. 5 min. After allowing the solution to quiet, 0.00 V *vs.* S.C.E. was applied (point C, Fig. 1) for approximately $^1/_2$ min, or until the potential of the mercury electrode *vs.* S.C.E., as measured independently, corresponded to the applied potential. The reason for applying this voltage is to reduce any mercurous chloride formed on the surface of the mercury through reaction with dissolved oxygen[2]. More reproducible results are obtained in this manner. The mercury pool was then polarized (see point D, Fig. 1) at the desired rate to an applied voltage of *ca.* + 1.4 V *vs.* S.C.E. The mercury chloride film is formed during this voltage scan interval. After reaching the applied voltage of + 1.4 V *vs.* S.C.E., the motor of the polarizing unit was reversed and the applied voltage returned to + 0.10 V *vs.* S.C.E. At + 0.10 V the film is not removed by cathodic reduction. Less than 5 μA of current was observed at this potential.

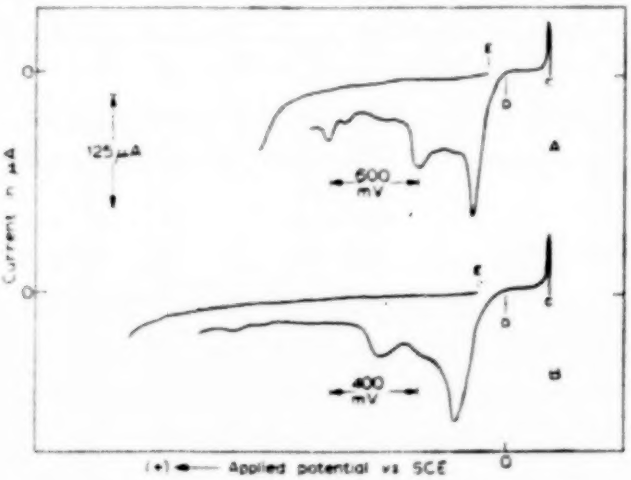

Fig. 1. Current–voltage curves for mercury chloride film formation and background re-scan. A. 600 mV/min. B. 400 mV/min.

The stock solution of the oxidizable substance was then added to the solution in the cell by a needle-tipped 10-ml buret which was inserted through a small hole in the top of the cell. Care must be taken during the addition to prevent any sharp jarring which may rupture the film surface. The solution was then stirred by nitrogen, allowed to quiet, and re-scanned from + 0.10 V to + 1.4 V *vs.* S.C.E. It is important that the applied voltage of + 0.10 V *vs.* S.C.E. be maintained during the interval between the first and second scans.

RESULTS AND DISCUSSION

Fig. 1, B shows a typical current–voltage (C–V) curve for the anodic polarization of the mercury pool electrode in the supporting electrolyte solution at a scan rate of 400 mV/min. The first large wave of *ca.* 120 μA peak anodic current is for the formation of mercurous chloride. Two other waves follow it whose half-peak potentials correspond closely to the quarter-wave potentials obtained by chronopotentiometry for the same chloride concentration and pH.

The peak current of the first wave is the point at which the freshly formed film first begins to limit the oxidation of mercury to mercurous chloride. The number of coulombs required to reach this state is reproducible from run to run within 5% and calculates to an initial film thickness of about 20 Å. The other waves which follow also contribute to the unique condition of passivation for the mercury electrode[3].

The re-scan of the electrode now called the Mercury Chloride Film Anode (MCFA) from +0.10 V *vs.* S.C.E., indicated in Fig. 1 by point E, to +1.4 V *vs.* S.C.E. gives a fairly flat "residual" current of *ca.* 5 μA. A background wave begins to appear at *ca.* 1.4 V *vs.* S.C.E. which is the useful limit of this electrode. The peak-type waves, representing film formation, are now absent on the re-scan. The potential of the MCFA *vs.* an auxiliary S.C.E. as measured independently follows the applied voltage within ±5 mV.

The level of the residual current varies between 5 and 10 μA from run to run depending on the polarization rate, the time required to return the applied voltage to +0.10 V *vs.* S.C.E. and the re-scan. The effect of the 600 mV/min scan rate on the film formation and re-scan waves may be seen in Fig. 1, A. Most work reported in this paper was performed at a scan rate of 400 mV/min.

The conditions of chloride concentration and pH favorable for film formation, and interferences from foreign ions and vibrations reported previously also apply here[1].

Oxidation of organic compounds

Curve B in Fig. 2 is for the oxidation of $3.8 \cdot 10^{-4} M$ solution of N,N-dimethyl-*p*-phenylenediamine (DPP) in the background electrolyte at a scan rate of 400 mV/min. The well defined peak-type wave (in an anodic direction) is similar to those obtained by STREULI AND COOKE[4] for voltage-scan polarography at a quiet mercury-pool electrode for the reduction of metal ions. Fig. 2, A shows the oxidation of 8-amino-1,3,6-naphthalenetrisulfonic acid (Koch's Acid).

Aniline, hydroquinone, and *p*-hydroxydiphenylamine gave similar peak-type waves as reproduced for 600 mV/min scan-rate in Fig. 3.

In this type of polarography the peak current is proportional to the concentration.

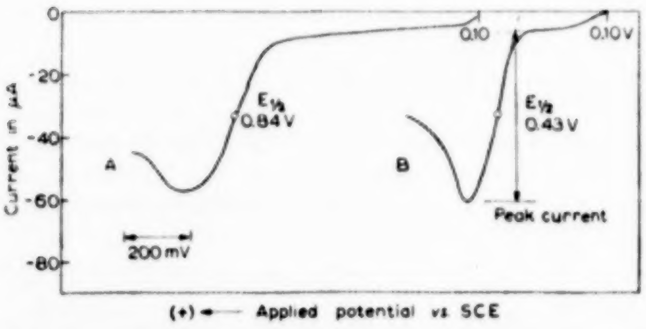

Fig. 2. Peak-type anodic C–V curves for oxidation at MCFA. A. $8.0 \cdot 10^{-4} M$ Koch's Acid. B. $3.8 \cdot 10^{-4} M$ DPP.

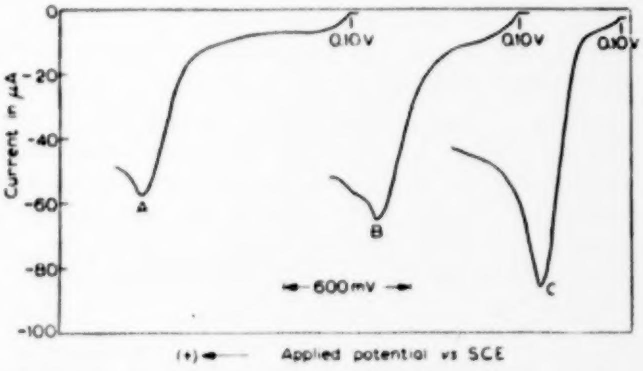

Fig. 3. Peak-type anodic C–V curves for oxidation at MCFA. A. $2.7 \cdot 10^{-4} M$ aniline. B. $4.1 \cdot 10^{-4} M$ hydroquinone. C. $6.0 \cdot 10^{-4} M$ *p*-hydroxydiphenylamine.

Aniline, hydroquinone, Koch's Acid, and DPP gave linear calibration curves in the concentration range of $10^{-4}M$ to $10^{-3}M$ solutions.

In conventional polarography at the dropping mercury electrode two procedures are generally used in correcting for the contribution of the residual current. One involves a subtraction of a previously recorded residual current. The other uses an extrapolation of the base line of the polarogram prior to the wave of the electroactive species. Since at the MCFA the residual current fluctuates a few μA from run to run, the latter method was selected. In applying this method, it was found empirically that more consistent results were obtained if the value of peak current (i_p) was determined as illustrated in Fig. 2, B. The variation of i_p/C was the least for this method of evaluating the peak current.

The values of i_p/C for DPP and Koch's Acid are summarized in Table I. The reproducibility is between 5 and 6%. There was a slight decrease in the value of i_p/C at higher concentrations.

TABLE I

VALUES OF CURRENT, HALF-PEAK POTENTIALS, AND NUMBER OF COULOMBS FOR FILM FORMATION

Concentration (mole/l)	i_p *(μA)*	i_p/C *(A/mole/l)*	E_p *(corrected)*[a]	*Coulombs*[b]
A. Koch's Acid: Background solution, 0.2*M* KCl, pH 2.7. Scanning rate 400 mV/min				
$2.51 \cdot 10^{-4}$	19.0	0.0757	+0.84	$7.9 \cdot 10^{-3}$
4.87	33.5	0.0687	0.85	7.1
7.10	47.2	0.0667	0.86	7.0
8.11	52.0	0.0640	0.88	7.1
9.20	58.0	0.0630	0.86	7.2
	Average	0.0676 ± 0.0037	0.86 ± 0.01	7.2 ± 0.2
	Deviation	5.5%	1%	3%
B. DPP: Background solution, 0.2*M* KCl, pH 2.4. Scanning rate 400 mV/min				
$1.96 \cdot 10^{-4}$	29.8	0.152	+0.49	$7.3 \cdot 10^{-3}$
3.23	43.5	0.138	0.46	7.2
5.06	68.0	0.134	0.45	7.4
6.83	87.2	0.128	0.45	8.0
8.00	99.2	0.124	0.46	8.2
	Average	0.135 ± 0.008	0.46 ± 0.01	7.6 ± 0.4
	Deviation	6%	2%	5%

[a] Corrected for *iR* drop. *R* as measured by AC bridge 620 ohms.

[b] Area under curve between 0.0 and 1.2 V *vs.* S.C.E. measured by planimeter. Number of coulombs calculated from area.

If the direction of the voltage-scan is reversed after the peak current is attained, and scanned in a less positive direction, a peak-type cathodic wave is observed for the reduction of the oxidized substance remaining near the electrode surface. Such a wave is shown for 3,3'-dimethylbenzidine (*o*-tolidine) in Fig. 4. Although no systematic study was undertaken to correlate these reverse waves, a general observation is that such waves only appear for compounds which behave in an approximately reversible manner at the platinum electrode. For compounds such as aniline and *o*-phenylenediamine which show irreversible behavior at the platinum electrode, no cathodic wave is observed prior to the reduction of the mercury chloride film.

Oxidation of inorganic compounds

Oxidation of ferrocyanide ion was not possible by chronopotentiometry because of mercurous ferrocyanide formation which prevented the mercury chloride film formation. In voltage-scan where the film is formed prior to the introduction of ferrocyanide, a double wave was observed. The first wave at *ca.* +0.15 V *vs.* S.C.E. is believed to be for the formation of insoluble mercurous ferrocyanide[5]. The second wave has a half-peak potential that corresponds to that obtained at the platinum electrode and is probably the oxidation of ferrocyanide to ferricyanide. The peak height of the second wave is proportional to the concentration of ferrocyanide.

No oxidation was observed for $10^{-3} M$ solutions of Co(II), Fe(II), and U(IV). Iodide and bromide ions form more insoluble salts with mercurous ion than chloride and remove the film. Visible crystals of mercurous iodide or bromide then appear on the surface of the mercury pool.

Oxidation-reduction of p-nitroaniline

The oxidation of the amino group in *p*-nitroaniline is difficult at a Pt electrode. The wave occurs at such positive potentials that it is merged with the background. Well defined oxidation waves are observed at the MCFA at about 1.1 V *vs.* S.C.E. While no extensive survey has been made, it is possible that oxidations which are difficult at Pt and Au electrodes may be accomplished at the MCFA.

It is evident that the MCFA, when stripped of its film can be operated as a conventional mercury pool cathode. The interesting possibility exists of carrying out both oxidations and reductions on the same solution. *p*-Nitroaniline has a reducible nitro group as well as the oxidizable amino function. It was found possible to first oxidize the amino group, then, after stripping the mercurous chloride film, reduce the nitro group. The ratio of oxidation to reduction current observed was approximately 1 to 10. The nitro reduction under these conditions is a 6-electron process[6].

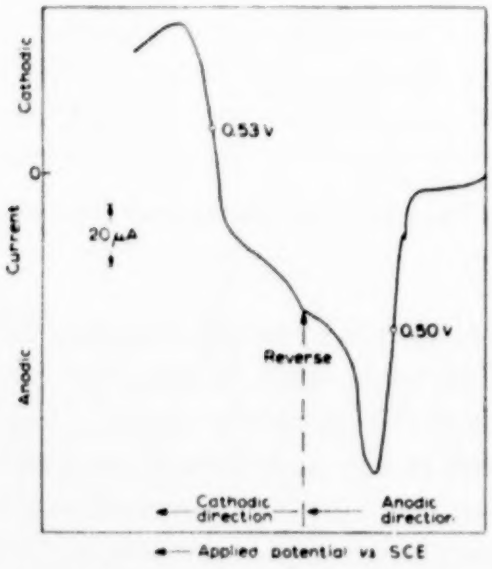

Fig. 4. Oxidation of 3,3'-dimethylbenzidine followed by reverse scan. Scanned anodically from right to left, reversed and scanned in a cathodic direction.

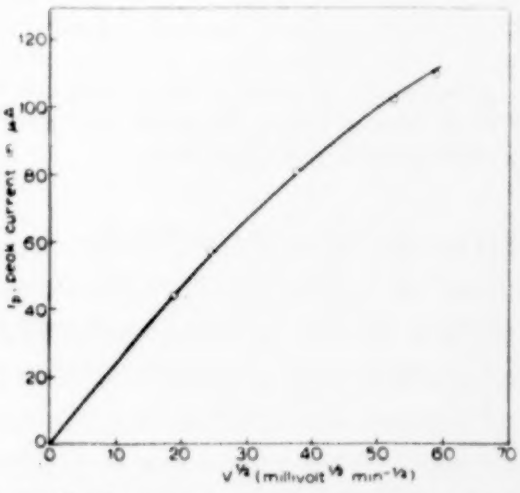

Fig. 5. Peak current *vs.* square root of scan rate. DPP concentration $3.2 \cdot 10^{-4} M$.

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Sensitivity

The sensitivity of the MCFA is about 10 fold greater by voltage-scan than chronopotentiometry. Further increase of sensitivity in conventional voltage-scan may be accomplished by increasing the area of the electrode, increasing the scanning rate, or by stirring the solution. The main limitation which determines the maximum sensitivity is still the ratio of the residual current to the peak oxidation current. A $10^{-4}M$ concentration of DPP gives approximately 14 μA current. This is about the lower limit of sensitivity where the residual current to the oxidation current approaches a 1:1 ratio.

In conventional quiet pool polarography[4] the peak currents are proportional to the square root of the scan-rate, $V^{1/2}$. This relationship also applies at the MCFA. Fig. 5 represents the experimentally determined curve of i_p *vs.* $V^{1/2}$ for $3.2 \cdot 10^{-4}M$ DPP in the background electrolyte. The value of i_p decreases at higher scan-rates. One possible reason for this decrease may be due to the larger iR drop which appears for the larger currents at higher scan-rates. The actual potential of the electrode then lags behind the applied potential.

Enhanced sensitivity may also be gained through stirring of the solution during the scan. Although sharp vibrations tend to rupture the film, mild stirring by nitrogen bubbling through a sintered glass deaerating tube can be tolerated. A preliminary experiment with stirring by nitrogen while oxidizing DPP indicates that at least a two fold increase in sensitivity is possible.

Reproducibility

The reproducibility of the peak current from day to day was checked for a period of a week at two scan-rates of 600 and 2800 mV/min. Fresh stock solutions of potassium chloride and DPP were prepared daily. The concentration of DPP was $3.2 \cdot 10^{-4}M$. The data are shown in Table II. In several instances, re-runs were made on the same MCFA and solution after stirring the solution by nitrogen and re-setting the applied voltage to +0.10 V *vs.* S.C.E. The day to day reproducibility for 9 runs is 4.4%. The reproducibility of 1–3 re-runs on the same MCFA and solution is between 2–4%.

The half-peak potential

The potential at the point where the current was one-half the peak value was designated as the half-peak potential, E_p.

The E_p values obtained at the MCFA for many organic compounds are in good agreement with $E_{1/2}$ values obtained at the Pt electrode under the same conditions of pH. The agreement of E_p values from run to run is *ca.* 2%. Table I gives the reproducibility of E_p values for changing concentrations of Koch's Acid and DPP. The values reported are corrected for iR drop of the circuit.

The E_p values determined at the MCFA are summarized in Table III. In the few cases where the agreement with the value obtained at the Pt electrode is poor, the E_p values are always shifted towards more positive potentials. Table III contains chronopotentiometric results at the MCFA and platinum electrodes for comparison.

Column 5 of Table I gives the total number of coulombs required for the formation of the film +0.00 to +1.2 V *vs.* S.C.E. prior to the oxidation of DPP and Koch's Acid.

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TABLE II

REPRODUCIBILITY OF PEAK CURRENTS

Concentration of DPP $3.2 \cdot 10^{-4} M$. Background electrolyte $0.2 M$ potassium chloride pH 2.5

i_p at 600 mV/min (µA)	*Re-runs* 1	*Re-runs* 2	*i_p at 2800 mV/min (µA)*	*Re-runs* 1	*Re-runs* 2	*Re-runs* 3
49.2			105.0	112.0	107.0	107.0
52.3			101.3	103.5		
54.0			101.4			
53.3	53.7		102.2	102.2	102.8	100.6
57.2						
58.0						
57.6						
52.7	56.9	59.0				
55.5	57.3	57.5				
Average 54.4 ± 2.4 Deviation 4.4%			Average 102.5 ± 1.3 Deviation 1.3%			

TABLE III

COMPARISON OF $E_{1/2}$ AND $E_{1/4}$ VALUES AT MCFA AND Pt ELECTRODE

Compound	*pH*	*Chronopotentiometry* $E_{1/4}$ *Pt*	*Chronopotentiometry* $E_{1/4}$ *MCFA*	*Polarographic* $E_{1/2}$ *Pt*	*Polarographic* E_p *MCFA*
DPP	2.7	0.41	0.37	—	0.43
	4.3	0.33	0.33	—	—
Aniline	2.7	0.85	—	—	0.85
	3.5	0.81	0.82	—	—
o-Phenylenediamine	4.0	—	0.43[a]	0.38[b]	—
	2.6	—	—	0.46[b]	0.70
p-Phenylenediamine	3.2	—	0.5	0.37[b]	0.63
Hydroquinone	2.7	0.42	0.95	—	0.61
p-Nitroaniline	2.6	N.P.[c]	—	—	1.1
p-Hydroxydiphenylamine	2.0	0.33	—	—	0.35
o-Tolidine	2.0	0.51	—	0.50	0.50
Koch's Acid	3.1	0.76	0.80	0.80[d]	0.78
H-Acid	2.7	—	—	0.73[e]	0.56
2,5-Dimercapto-1,3,4-thiadiazole	2.6	—	—	0.20	*ca.* 0.66[a]
1,10-*o*-Phenanthroline ferrous	3.5	1.10	0.96	1.05	—
Ferrocyanide	2.7	0.40	N.P.[f]	—	0.40
Ferrous ion			N.O.[g]		N.O.
Cobalt(II)			N.O.		N.O.
Uranium(IV)			N.O.		N.O.
Iodide ion			N.P.		N.P.

[a] Poorly defined wave.
[b] Data of PARKER AND ADAMS[7].
[c] Not Possible (N.P.): oxidation wave merges with background wave.
[d] Value at pH 9.0.
[e] Value at pH 1.2.
[f] Ferrocyanide interferes with film formation due to reaction with mercurous ion.
[g] No Oxidation Observed (N.O.).

It may be seen that the E_p's are independent of the number of coulombs required for the film.

Occasionally, perhaps one out of every 10 runs, the film formation waves were large. Since the E_p values become dependent on the film thickness above a certain maximum, an arbitrary upper limit of $10 \cdot 10^{-3}$ coulombs was set for the film formation wave. This corresponded to a maximum peak current for the first film wave of 200 μA using a scan-rate of 400 mV/min.

The presence of surface-active agents interfere markedly with the film formation waves. Gelatine, methyl red, Koch's Acid, and other surface-active agents may be introduced only after the film is formed. This was the reason why Koch's Acid could not be determined at higher concentrations by the chronopotentiometric method.

ACKNOWLEDGEMENTS

The authors are grateful to the Research Corporation of America for a grant in partial support of this work. The authors gratefully acknowledge the sample of pure *p*-hydroxydiphenylamine from John McCarty, samples of Koch's and H-Acid from E. I. du Pont de Nemours and Company, and the 2,5-dimercapto-1,3,4-thiadiazole from the B. F. Goodrich Company.

We are indebted to R. T. IWAMOTO for his helpful suggestions during the course of this work, and to MARTHA KELLY for assistance in preparing the manuscript.

SUMMARY

The Mercury Chloride Film Anode (MCFA) is proposed as a working anode which may have desirable properties for oxidation of organic molecules. For many organic molecules it shows characteristics comparable to the platinum electrode.

It has a higher background overvoltage than the platinum electrode. The polarographic wave of *p*-nitroaniline is not obtained at a platinum electrode. A well-defined wave is observed at the MCFA at *ca.* 1.1 V *vs.* saturated calomel electrode.

The sensitivity of the MCFA by voltage-scan is some 10 fold greater than that of chronopotentiometry. Preliminary experiments indicate that sensitivity may be enhanced by stirring of the solution.

RÉSUMÉ

Une anode à film de chlorure de mercure est proposée pour l'oxydation de molécules organiques. La sensibilité par ,,voltage-scan'' est environ dix fois plus grande que celle obtenue par chronopotentiométrie. Des expériences préliminaires montrent que la sensibilité peut être améliorée par agitation de la solution.

ZUSAMMENFASSUNG

Die Quecksilberchloridfilm-Anode lässt sich zur anodischen Oxydation von organischen Substanzen verwenden. Die Empfindlichkeit durch ,,Voltage-Scan'' ist ungefähr 10 mal grösser als die bei chronopotentiometrischen Messungen. Versuche haben gezeigt, dass die Empfindlichkeit durch Rühren der Lösung noch gesteigert werden kann.

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SEPARATIONS INVOLVING SULPHIDES

VIII. SEPARATION OF RUTHENIUM AND INDIUM FROM ALKALINE EARTH METALS

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Methods for the quantitative separation of alkaline earths from a number of elements forming thiosalts or sulphides, with $2N$ sodium sulphide reagent[1] have already been proposed in a previous publication[2]. In this paper similar procedures for estimating ruthenium or indium in the presence of alkaline earths are given.

EXPERIMENTAL

Separation of ruthenium from alkaline earths

Measured volumes of standard solutions of ruthenium chloride[3] (prepared with dilute hydrochloric acid) and barium chloride[4], strontium chloride[5], calcium chloride[6] or magnesium chloride[7] were mixed and treated with ammonium hydroxide till a slight turbidity appeared. The mixture was treated with 40–50 ml of $2N$ sodium sulphide reagent followed by enough $6N$ acetic acid to give an acidity of about $3N$ and then 10–15 g of ammonium acetate were added. The mixture was heated to boiling and allowed to cool to room temperature. The precipitate of ruthenium sulphide was filtered through a weighed sintered glass crucible (porosity 4), washed thoroughly with distilled water (the filtrate being reserved for the estimation of alkaline earths), alcohol and ether successively, dried in vacuum for half an hour and weighed as $Ru_2S_3 \cdot 2H_2O$.

The filtrate was boiled to expel hydrogen sulphide etc., the free acid neutralized with ammonia (sp.gr. 0.88), and diluted to 250 ml.

Barium or strontium were estimated as sulphate.

Calcium was precipitated as oxalate and estimated as $CaCO_3$.

Magnesium was precipitated as magnesium ammonium phosphate and estimated as $Mg_2P_2O_7$.

In the estimation of calcium or magnesium reprecipitation is essential to get satisfactory results.

28–36 mg of ruthenium could be separated from 55–70 mg of barium, 34–44 mg of strontium, 72–90 mg of calcium or 12–16 mg of magnesium. The metals were recovered with an accuracy of:

Ru +0.14 to −0.33% and Ba +0.1 to −0.16%;
Ru 0.0 to −0.24% and Sr 0.0 to −0.14%;
Ru 0.0 to −0.24% and Ca 0.0 to −0.12%;
Ru +0.14 to −0.24% and Mg 0.0 to −0.31%.

Separation of indium from alkaline earths

Standard solutions of indium chloride[8], barium chloride, strontium chloride, calcium chloride and magnesium chloride were used. The procedure given for the separation of ruthenium from alkaline earths was followed. The precipitate of indium sulphide was washed with hot 3*N* acetic acid (to prevent peptization) and then with alcohol and ether successively. Indium was estimated as In_2S_3.

In the filtrate barium or strontium was estimated as sulphate, calcium as carbonate and magnesium as pyrophosphate.

22-30 mg of indium could be separated from 57-72 mg of barium, 34-44 mg of strontium, 40-50 mg of calcium or 12-16 mg of magnesium. The metals were recovered with an accuracy of:

In 0.0 to —0.24%, Ba 0.0 to —0.23% and Sr 0.0 to —0.21%;
In +0.29 to —0.22% and Ca 0.0 to —0.32%;
In 0.0 to —0.22% and Mg 0.0 to —0.32%.

SUMMARY

It has been shown that 2*N* sodium sulphide reagent can be efficiently used for separating ruthenium or indium from alkaline earth metals.

RÉSUMÉ

On a utilisé avec succès le sulfure de sodium 2*N* pour la séparation du ruthénium ou de l'indium d'avec les métaux alcalino-terreux.

ZUSAMMENFASSUNG

Es wird gezeigt, dass eine 2*N* Natriumsulfidlösung zur Trennung von Ruthenium oder Indium von den Erdalkalimetallen verwendet werden kann.

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SEPARATIONS INVOLVING SULPHIDES

IX. SEPARATIONS OF ALKALINE EARTH METALS FROM SOME ELEMENTS THAT FORM THIOSALTS

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The work discussed in this series of papers, has been divided into three sections under the headings indicated in an earlier publication[1]. Some separations of alkaline earth metals coming under the first heading have been dealt with in two papers already published[1,2]. In this paper the remaining separations of alkaline earth metals from elements that form thiosalts are dealt with.

EXPERIMENTAL

Separation of arsenic, antimony, tellurium, selenium or molybdenum from strontium

Standard solutions of sodium arsenate, potassium antimony tartrate, potassium tellurite, selenious acid, ammonium molybdate and strontium chloride were used. Measured volumes of the two solutions were mixed together. The mixture was treated with 2*N* sodium sulphide reagent in excess. The solution containing the thiosalt was acidified with a measured quantity of hydrochloric acid. The mixture was heated to boiling and allowed to cool to room temperature. The precipitate was filtered through a weighed sintered glass crucible (porosity 4), and the metals were estimated as As_2S_5[3], Sb_2S_3[4], TeS_2[3], SeS_2[3] or $MoS_3 \cdot 2H_2O$[5] respectively.

The following points must be borne in mind when precipitating the different sulphides.

(1) If a white precipitate appears on mixing the two solutions, it should be dissolved in the minimum quantity of dilute hydrochloric acid.

(2) In the case of molybdenum sufficient acid should be present in the solution to which sodium sulphide is added and the reagent should be added dropwise with constant shaking, otherwise molybdenum blue may form and pass into the filtrate.

(3) The solution containing the thiosalt of arsenic should be acidified with a measured volume of concentrated hydrochloric acid, to produce an acidity of approximately 6*N* in the resulting mixture. In the case of other elements the solution containing the thiosalt is acidified with 2*N* hydrochloric acid to produce an acidity of approximately 1*N* in the resulting mixture.

(4) In the case of selenium a more easily filterable precipitate is obtained, if the concentration of the acid in the resulting mixture is about 4*N*. After acidification the mixture should not be boiled. It should be kept at a lower temperature (70°–80°), until the yellow precipitate becomes orange in colour.

(5) The caustic soda solution used in preparing the sodium sulphide reagent should be free from silica, which is sometimes extracted from the glass bottle in which it is preserved.

After filtering off the sulphide, the filtrate was evaporated to about 50 ml to remove hydrogen sulphide, the free acid neutralized with ammonia (sp.gr. 0.88), the solution diluted to about 250 ml and strontium estimated as $SrSO_4$[6].

39–40 mg of arsenic were separated from 45–47 mg of strontium.
59–61 mg of antimony were separated from 45–46 mg of strontium.
59–60 mg of tellurium were separated from 45–46 mg of strontium.
53–60 mg of selenium were separated from 45–50 mg of strontium.
51–53 mg of molybdenum were separated from 45–46 mg of strontium.

The metals were recovered with an accuracy of:

As −0.28% to +0.4%	Sr −0.2% to +0.4%
Sb −0.23% to +0.3%	Sr 0.0% to +0.4%
Te −0.21% to +0.08%	Sr ±0.39%
Se 0.0% to +0.29%	Sr −0.5% to 0.0%
Mo −0.19% to +0.17%	Sr −0.3% to 0.0%

Separation of arsenic, antimony, tellurium, selenium or molybdenum from calcium

Standard solutions of sodium arsenate, potassium antimony tartrate, potassium tellurite, selenious acid, ammonium molybdate and calcium chloride were used. Measured volumes of the two solutions were mixed together. The procedure given for the separation of these metals from strontium was followed. As, Sb, Te, Se or Mo were estimated as sulphides. After filtering off the sulphide the filtrate was evaporated to about 50 ml to remove hydrogen sulphide, the free acid neutralized with ammonia (sp.gr. 0.88), and the solution diluted to about 250 ml. Calcium was precipitated as oxalate. Reprecipitation was necessary to get satisfactory results. Calcium was estimated as $CaCO_3$[7].

39–40 mg of arsenic were separated from 45–46 mg of calcium.
59–60 mg of antimony were separated from 45–46 mg of calcium.
42–57 mg of tellurium were separated from 45–51 mg of calcium.
54–56 mg of selenium were separated from 45–46 mg of calcium.
39–53 mg of molybdenum were separated from 32–46 mg of calcium.

The metals were recovered with an accuracy of:

As −0.47% to +0.1%	Ca −0.42% to 0.0%
Sb −0.15% to +0.23%	Ca −0.35% to 0.0%
Te −0.33% to +0.35%	Ca −0.5% to 0.0%
Se 0.0% to +0.5%	Ca −0.5% to +0.2%
Mo −0.078% to +0.37%	Ca −0.5% to +0.27%

Separation of arsenic, antimony, tellurium, selenium or molybdenum from magnesium

Standard solutions of sodium arsenate, potassium antimony tartrate, potassium tellurite, selenious acid, ammonium molybdate and magnesium chloride were used. Measured volumes of the two solutions were mixed. The procedure given for the separation of these metals from strontium was followed. The metals were estimated as sulphides. After filtering off the sulphide the filtrate was evaporated to about 50 ml to

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remove hydrogen sulphide, the free acid neutralized with ammonia (sp.gr. 0.88), and the solution diluted to about 250 ml. Magnesium was precipitated as $MgNH_4PO_4 \cdot 6H_2O$. Reprecipitation was necessary to get satisfactory results. Magnesium was estimated as $Mg_2P_2O_7$[8].

32–63 mg of arsenic were separated from 21–22 mg of magnesium.
58–59 mg of antimony were separated from 21–22 mg of magnesium.
42–55 mg of tellurium were separated from 21–24 mg of magnesium.
53–60 mg of selenium were separated from 21–28 mg of magnesium.
40–50 mg of molybdenum were separated from 21–45 mg of magnesium.

The metals were recovered with an accuracy of:

As	—0.5% to 0.0%	Mg	—0.39% to 0.0%
Sb	—0.39% to 0.0%	Mg	—0.42% to +0.4%
Te	—0.4% to 0.0%	Mg	0.0% to +0.7%
Se	—0.4% to +0.18%	Mg	—0.4% to 0.0%
Mo	—0.15% to 0.0%	Mg	—0.4% to +0.5%

Note: It has not been found possible to estimate tin in presence of alkaline earth metals by decomposing the thiosalt, owing to the tendency of stannic sulphide to peptize on washing.

SUMMARY

It has been shown that 2*N* sodium sulphide reagent can be used for separating strontium, calcium or magnesium from arsenic, antimony, tellurium, selenium or molybdenum.

RÉSUMÉ

Le sulfure de sodium 2*N* peut être utilisé pour la séparation du strontium, du calcium ou du magnésium d'avec l'arsenic, l'antimoine, le tellure, le sélénium ou le molybdène.

ZUSAMMENFASSUNG

Es wird gezeigt, dass eine 2*N* Natriumsulfidlösung zur Trennung von Strontium, Calzium oder Magnesium von Arsen, Antimon, Selen oder Molybdän verwendet werden kann.

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THE PALLADIUM ELECTRODE IN AQUEOUS AND NONAQUEOUS TITRIMETRY

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SCHWING AND ROGERS[1] have pointed out the uncertain state of the literature concerning the reliability of the palladium-hydrogen electrode. These workers studied the behavior of various forms of electrode and found the most satisfactory type to be one involving a palladium membrane on which hydrogen was generated continuously. They also made a few titrimetric studies in 75% ethanol. Earlier SANDVED AND HARANG[2] employed a concentration cell consisting of two palladium hydride electrodes for the potentiometric titration of a variety of bases dissolved in ethanol or acetone. The present work concerns our attempts to improve the design for the electrode recommended by SCHWING AND ROGERS and to develop a completely new form of "generation" electrode. This latter form is simple to construct, gives results of satisfactory reproducibility, responds rapidly, and was first tested in aqueous systems. Experiments in the field of nonaqueous titrimetry[3] gave useful results.

Reagents and apparatus

In much of the work, buffer solutions made from "pHydrion**" capsules were used. In other cases, McIlvaine buffers adjusted with potassium chloride to a constant ionic strength of 0.5*M* were employed[4]. All pH values were checked by a Leeds and Northrup Model 7664 pH Meter. Most of the organic solvents and reagents were "White Label" from Eastman Kodak Company, and were used without further treatment.

The palladizing solution used was 2% palladous chloride in 1*N* hydrochloric acid. A current density of 40–50 mA/cm^2 was employed in the deposition of the palladium black.

Potential measurements were made with a Beckman Model G pH Meter and saturated calomel electrode. All studies were carried out at room temperature, and with air-containing solutions.

RESULTS

Modifications of the Schwing and Rogers type electrode

To permit the easy interchange of different palladium diaphragms, the cement-mounting technique of SCHWING AND ROGERS was replaced by one in which the disc was gripped between two rubber "O"-rings. The arrangement is shown in Fig. 1. The electrode vessel, A, is a 25×80 mm screw-capped sample tube from which the bottom has been removed. The plastic cap, B, has a 15 mm central hole which permits palladium diaphragm, C, of thickness 0.12 mm, to come in contact with the test solution. To minimize the accumulation of gas bubbles on the underside of the diaphragm, two pairs of wide grooves are filed nearly through the thickness of the cap as shown at (a). Into a small hole in the side of the cap was cemented 1/8-inch diameter polyethylene tubing, D, which was bent upwards and allowed a platinum connecting wire, E, to be kept out of contact with the solution. The inner end of the wire was flattened so that it could be gripped between the upper rubber ring, F, and the palladium disc. Supported by a grooved stopper, auxiliary electrode, G, is a 5-cm length of 24-gauge platinum wire wound into a spiral. This platinum wire was sealed through the end of a length of glass tubing so that contact could be made to the copper connecting wire by means of a column of mercury. The electrode vessel contained decinormal sulfuric acid. The auxiliary electrode was connected through a milliammeter and a variable resistor to the positive pole of a dry battery. The negative pole of the battery was connected to platinum lead, E. The latter was also connected to the "glass electrode" pin of the pH meter while the other pin led to the saturated calomel reference electrode. The small voltage correction introduced by the resistance of the platinum lead was allowed for.

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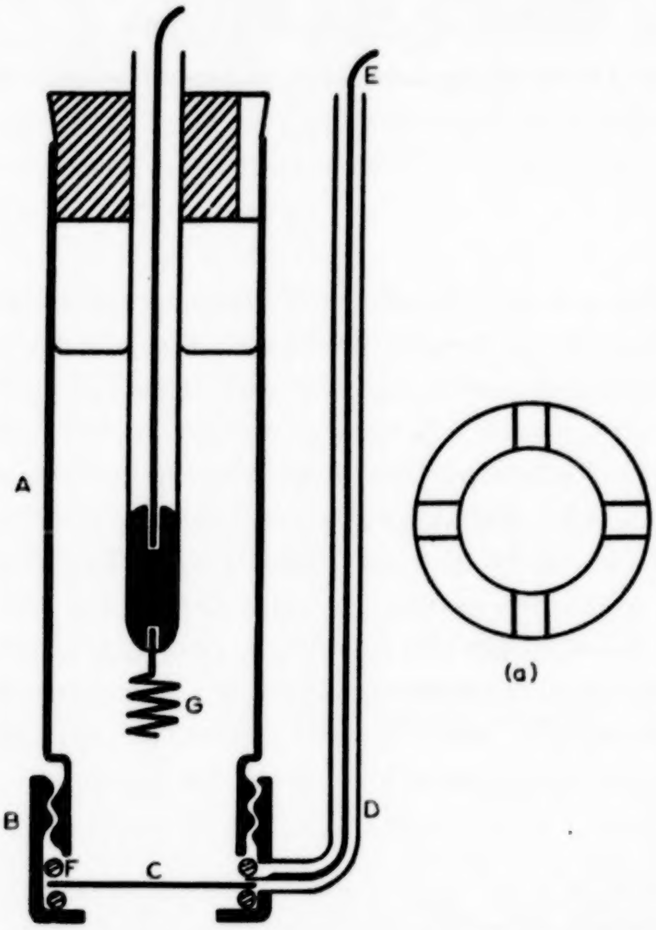

Fig. 1. Diaphragm-type palladium electrode.

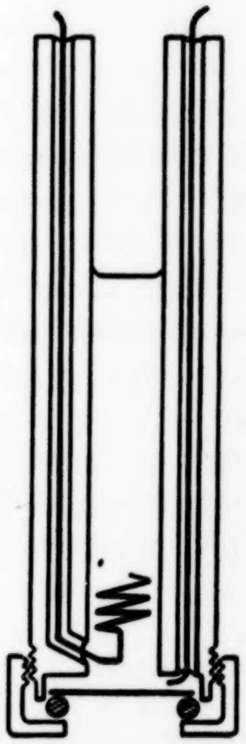

Fig. 2. Electrode constructed from Lucite rod.

A smaller form of electrode was constructed from a lucite rod. General details are shown in Fig. 2. The principal difference in design is that the leads to the disc and to the auxiliary electrode pass down holes drilled in the wall thickness. These holes were subsequently filled with liquid cement which was allowed to harden before the electrode was used.

Most of the experiments were, however, made with the electrode shown in Fig. 1. The results obtained in the measurement of the pH of aqueous buffers and in acid-base titrations closely paralleled those reported by SCHWING AND ROGERS. A generating current of 5 mA, corresponding to a current density of about 2.5 mA/cm² on the inner side of the disc, was used initially. Numerous experiments in which the current density was varied between 0.5 and 10.0 mA/cm² indicated the desirability of operating at small values. This minimizes gas formation on the surface of the disc, appears to reduce the stabilization time, and gives steadier readings. The sensitivity of the e.m.f. measurements to stirring found by SCHWING AND ROGERS was also noted.

The circulating palladium electrode

Owing to the uncertain readings obtained with palladium electrodes of the type described above, experiments were made to develop an electrode of radically different design. The desired features were (1) a vertical diaphragm to avoid entrapment of hydrogen bubbles (2) the elimination of joints which needed to be watertight, and (3) the introduction of powerful constant stirring which would give constant potentials. The last feature is essential for the plotting of potentiometric titration curves while the well-known changes in dimensions undergone by palladium when it absorbs or desorbs hydrogen cause the buckling of a tightly held disc.

These features are incorporated in the electrode shown in Fig. 3. Electrode tube, H,

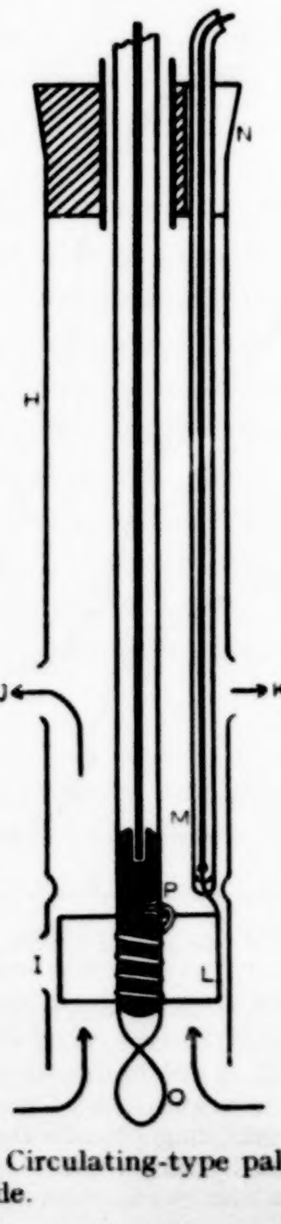

Fig. 3. Circulating-type palladium electrode.

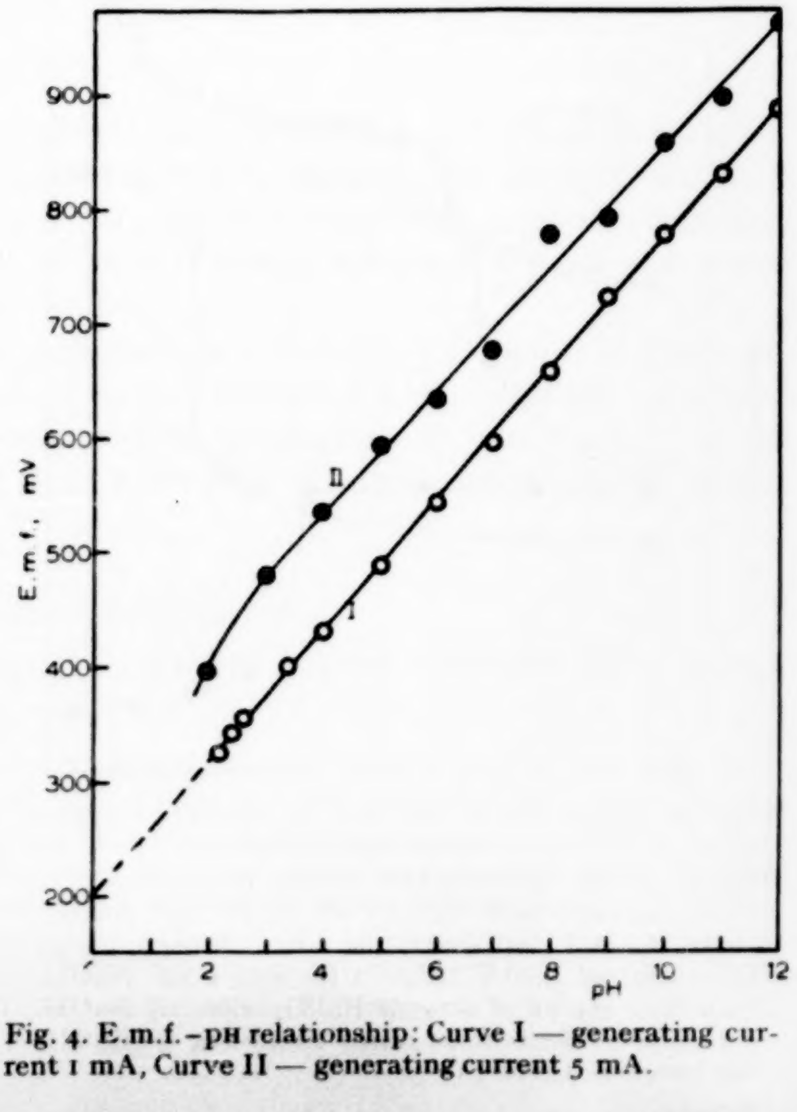

Fig. 4. E.m.f.-pH relationship: Curve I — generating current 1 mA, Curve II — generating current 5 mA.

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is 20 mm in diameter and 100 mm long. Three six-mm holes, I, J, and K, are blown in the wall as shown and the tube is crimped as shown about 20 mm from the lower end. The crimp serves to locate the palladium foil electrode, L, which is a rectangle 10 × 40 mm and has a small projecting tongue on one of the longer sides. A platinum connecting wire is welded to this tongue and a polyethylene-tubing sleeve, M, is slipped over the joint as shown, the lower end being closed by cementing. For studies in nonaqueous media, "Teflon" or glass tubing should replace polyethylene. After palladizing both sides of the rectangle, it is coiled up to form a nearly complete cylinder and sprung into the electrode tube from the bottom. The gap in the cylinder should be about diametrically opposite to hole I. The upper end of the polyethylene tubing is lightly gripped in grooved cork, N, which also carries a loosely-fitting glass guide cylinder for the rotating auxiliary electrode. This is constructed of 6-mm diameter glass tubing, carries at its lower end a spiral stirrer, O, and is driven by a Sargent Synchronous Rotator at a constant rate of 600 r.p.m. The auxiliary electrode proper consists of a close four-turn spiral of 24-gauge platinum wire, one end of which is sealed through the wall of the

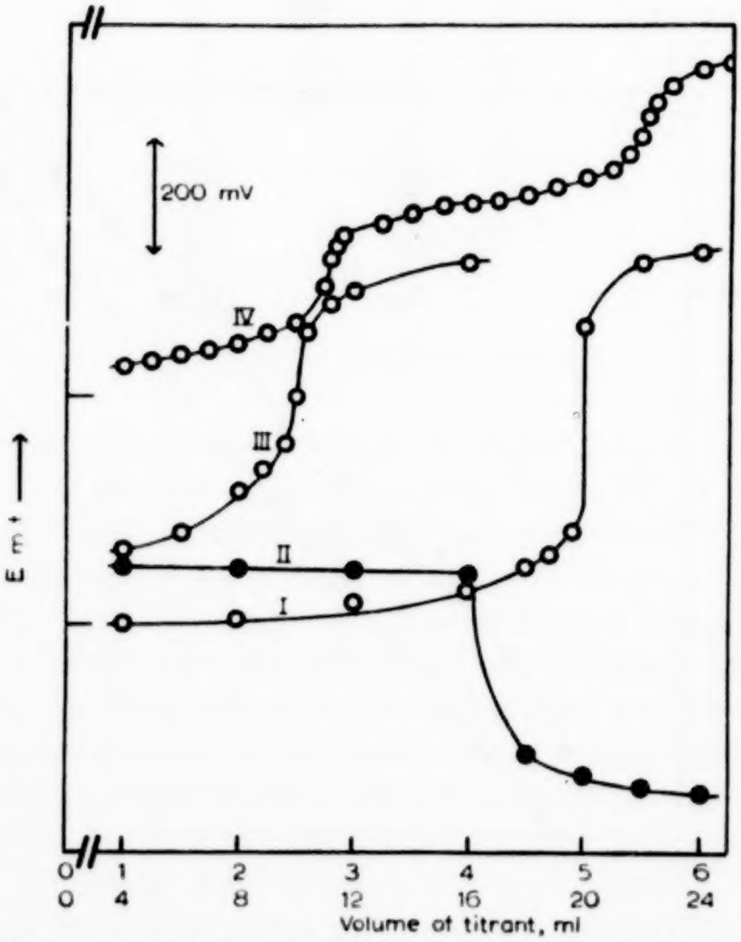

Fig. 5. Acid–base titration curves in aqueous medium: Curve I - 50 ml of 0.1N HCl with 1.0N NaOH, Curve II - as I, but generating circuit broken, Curve III - 25 ml of 0.01N CH_3COOH with 0.1N NaOH, Curve IV - 25 ml of 0.147M H_3PO_4 with 1N NaOH. The upper volume scale refers to curves I, II, III, the lower to curve IV.

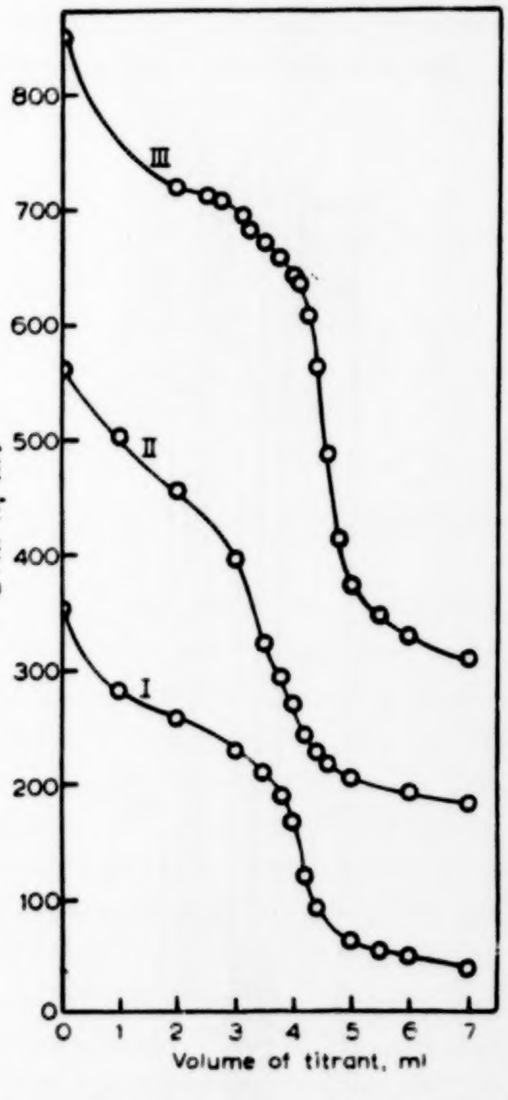

Fig. 6. The nonaqueous titration of 25 ml of approximately 0.02N triethylamine with 0.1N hydrochloric acid: Curve I - in acetonitrile, Curve II - in ethanol containing 5% of water, Curve III in dimethylformamide.

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tube at P. Connection to this electrode is made in the usual way by means of a mercury column. The electrical connections are essentially the same as those described for the electrode shown in Fig. 1.

Studies in aqueous solutions

To assess the likely performance in titrimetry, the electrode assembly shown in Fig. 3 was immersed successively in a series of buffer solutions and the e.m.f. was measured 2 min later. After removal from one buffer, the system was rinsed with distilled water and introduced into the next buffer. As noted with the horizontal palladium diaphragm electrodes, use of a low current density is beneficial. This is illustrated in Fig. 4, which clearly shows the scattered results obtained with a generating current of 5 mA and the improvement effected by reducing the current to 1 mA. In the latter case, the slope, namely 57.6 mV per pH, approximates quite closely the theoretical value. On extrapolation to pH 0, the standard potential referred to the S.C.E. is 200 mV. Correcting to the hydrogen scale, this value agrees well with that found for saturated α-palladium in hydrogen stirred solutions[5,6].

Numerous acid-base titrations were then performed using a generating current of 1 mA. Typical titration curves are given in Fig. 5. It was found that e.m.f. readings could be taken within 1 min after each addition of reagent. When the generating current is cut off, the electrode soon fails to respond satisfactorily. This is clear from a comparison of curves I and II which both refer to the titration of 0.1 *N* hydrochloric acid.

Studies in nonaqueous media

Titrations of a variety of weak and strong acids dissolved in 95% ethanol gave satisfactory curves when titrated with decinormal sodium methoxide in absolute methanol. A generating current of between 0.1 and 0.2 mA was found to be satisfactory in most of the nonaqueous titrimetry. The results were erratic with succinic acid and others which gave precipitates during the titration.

Titrations of organic bases were performed in a variety of solvents; of these, dimethylformamide appears to be the most satisfactory (Fig. 6). Attempts to titrate organic acids in ethylenediamine with sodium aminoethoxide solution have so far proved unsatisfactory. In some of these attempted titrations, a visible film formed on the palladium surface.

ACKNOWLEDGEMENT

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SUMMARY

Two modifications of the palladium–hydrogen electrode of SCHWING AND ROGERS have been made and tested. A new form of "generation" electrode with a vertical palladium diaphragm and fast constant speed circulation has been devised. This form of electrode responds rapidly and has been used in a variety of acid–base titrations in aqueous and nonaqueous systems.

RÉSUMÉ

Deux modifications ont été apportées à l'électrode palladium–hydrogène de SCHWING ET ROGERS. Cette nouvelle forme d'électrode peut être utilisée pour de nombreux titrages acide–base en solutions aqueuses et non aqueuses.

ZUSAMMENFASSUNG

Es werden 2 Modifikationen der Palladium-Wasserstoff Elektrode nach SCHWING UND ROGERS beschrieben. Mit der neuen Elektrodenform können zahlreiche Säure-Basen Titrationen in wässrigem und nicht-wässrigem Medium ausgeführt werden.

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THE PHOTOMETRIC DETERMINATION OF SILICON AS α-SILICOMOLYBDIC ACID

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An accurate and at the same time rapid method for the determination of silicon has long been needed by the analysts. Accurate gravimetric methods are too laborious, and rapid gravimetric or titrimetric methods do not give satisfactory results. Therefore, in the last years, photometric methods have often been suggested.

The accuracy of photometric measurement is now so high that also the main components of a mixture can be determined with relative errors of a few tenths of a per cent or less. However, this accuracy is delusive if the method is not based on sound chemical principles. Above all, the color must be quite stable and reproducible.

Existing photometric methods for the determination of silicon are based on the utilization of either the yellow color of silicomolybdic acid or the blue color of reduced silicomolybdic acid. A critical examination of the procedures described in the literature does not give very encouraging results. (For references, see JEAN[1,2] where a list of papers is given.) The color always depends on the experimental conditions, particularly the acidity and the excess of the reagent, and a perfect reproducibility is difficult to attain. As a rule, the colors obtained are not stable; the intensity varies with time.

An explanation for this behavior was given by STRICKLAND[3], who in 1952 reported the results of a careful investigation of the formation of silicomolybdic acid. He showed that two modifications of this acid exist: an α acid formed at low acidities and a β form formed at high acidities. The α form is the stable form, and the β compound changes more or less rapidly into the α form. Using light with a wave-length of approximately 400 mμ, the absorbance index of the β form is about twice the index of the α form.

Reducing agents convert both forms into blue-colored products. However, the colors differ considerably; the α product is greenish blue whereas the β product is deep blue.

As far as we have found, all procedures given in the literature are based on reactions leading to the β form*, but since this form is not stable, smaller or larger amounts of the α form are always present. Therefore, it is not surprising that the colors — the yellow as well as the blue ones — are usually neither sufficiently stable nor sufficiently reproducible for the attainment of a high precision in analysis.

From the point of view of the analyst, it seems that the logical deduction from STRICKLAND's observations should be that the α form is superior as the basis of a photometric method. A procedure leading to this form seems to provide a solution of the problem of developing a rapid, precise method for the determination of silicon. The higher absorbance index of the β form is sometimes considered as a particular advantage. However, if silicon is one of the main components, the stability and reproducibility of the color is more important than a slightly higher sensitivity. Moreover, the absorbance index of the β form is greater than the index of the α form only at wave-lengths above 340 mμ, whereas at shorter wave-lengths the α form absorbs more light. In most analyses a reduction of the yellow form is unnecessary.

The results of some experimental investigations will be reported in the following.

EXPERIMENTAL CONDITIONS LEADING TO THE FORMATION OF THE α ACID

According to STRICKLAND, both silicomolybdic acids have the formula $H_4SiMo_{12}O_{40}$. STRICKLAND has also determined the absorption spectra of the two forms, and our results were in good agreement with his values. The two curves intersect at 340 mμ as can be seen in Fig. 1.

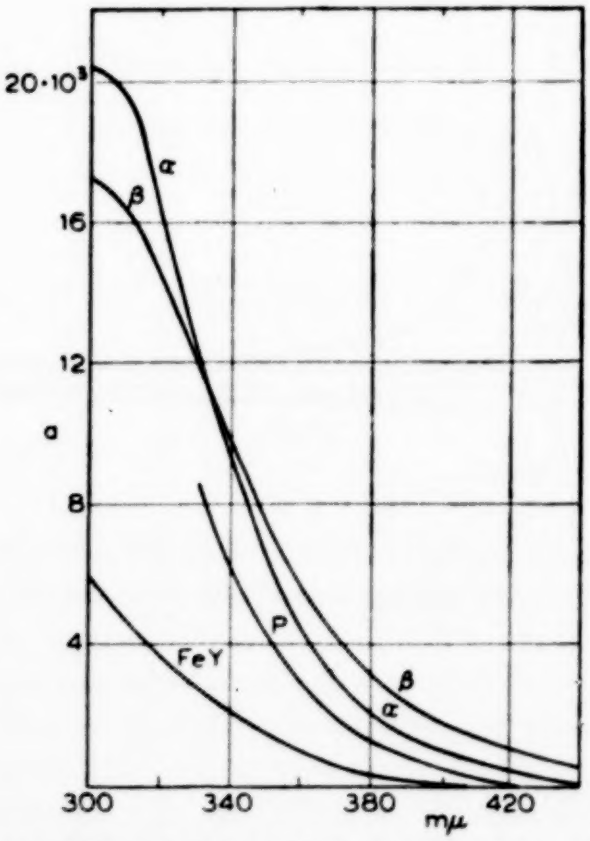

Fig. 1. Absorbance indices of α-silicomolybdic acid, β-silicomolybdic acid, phosphomolybdic acid, and Fe(III)-EDTA as functions of the wave-length.

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* Note added in proof: In a recent paper by ANDERSSON[6] also a method based on the color of the α acid is described.

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The problem of the structure of the two forms will not be discussed in this paper. It may only be mentioned that the two modifications are probably derived from the two polynuclear molybdate ions formed on acidification. According to LINDQVIST[4] MoO_4^{-2} ions are stable at pH > 6.5. At pH ∾ 4.5, paramolybdate ions $Mo_7O_{24}^{-6}$ are formed, which are transformed into octamolybdate ions $Mo_8O_{26}^{-4}$ in the pH range 2.9–1.5. It seems likely that the α acid is formed from the paramolybdate and the β acid from the octamolybdate.

Systematic investigations of the formation of the yellow compounds led to the following results:

1. In very acid solutions (pH < 2.5) the reaction between silica and ammonium molybdate results in a yellow color, which gradually fades.

2. In very weakly acid solutions (pH > 4) a yellow color is produced which gradually becomes more intense.

3. At pH values between 2.3 and 3.9 a yellow color is formed which slowly changes in intensity — it usually decreases, but increases at the upper limit of the pH range — and attains a constant value after 1/2 to 12 hours depending on the pH (Fig. 2). For a certain concentration of silicon the final absorbance value is always the same. The reaction [illegible] accelerated by a rise in temperature. Heating to 100° is usually enough for the rapid attainment of equilibrium. If the solution is made strongly acid after the equilibrium state has been reached, no change in the color will occur.

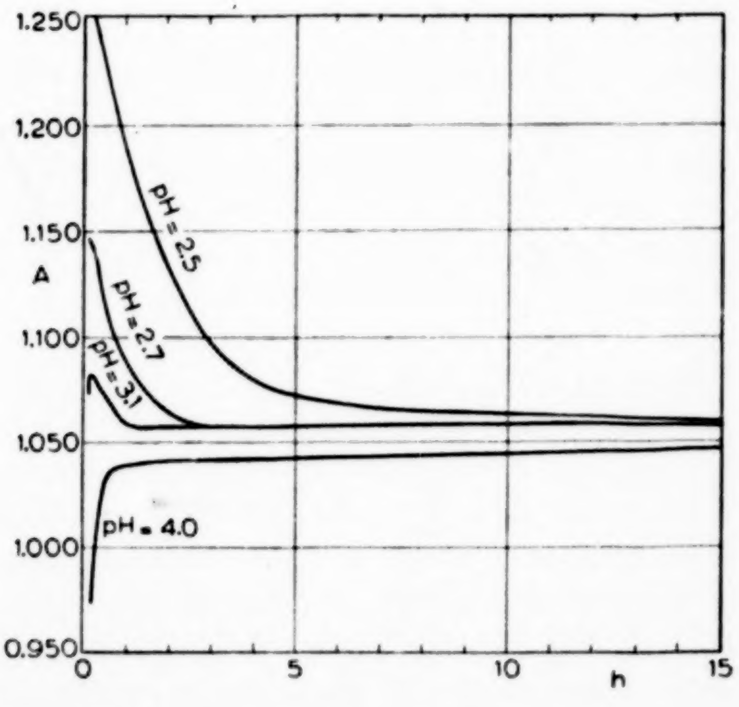

Fig. 2. Change of absorbance with time in hours at various pH values.

These results can easily be interpreted on the basis of STRICKLAND's investigations. At low acidities, the α acid is formed, but at pH values above 3.9, the reaction is incomplete. At pH values below 2.3, the β acid is formed, which very slowly goes over into the α form.

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It seems clear that the most favorable conditions for a photometric method based on the color of the *α* form exist in the pH range 2.3–3.9. Various buffer substances have been tried. Formic acid-formiate was used in many experiments, but since this buffer exhibited reducing properties, a monochloracetic acid-monochloracetate buffer was later preferred. The dissociation constant of this acid is $10^{-2.9}$.

Fig. 3 illustrates the dependence of the reaction on pH.

The curve shows a plateau at pH 2.1–3.9.

The influence of the concentration of molybdate was also investigated. Twice the theoretically required amount is sufficient to produce the final absorbance value. However, the required minimum concentration of molybdate depends somewhat on the acidity. At low pH values, a larger excess of molybdate is required.

The absorbance values obtained when the given procedure is followed are stable and reproducible, but they depend on the temperature of the solution. Several series of experiments gave a rather high temperature coefficient of 0.39% per degree centigrade. It is therefore necessary either to determine the absorbance at a constant temperature or to apply a temperature correction.

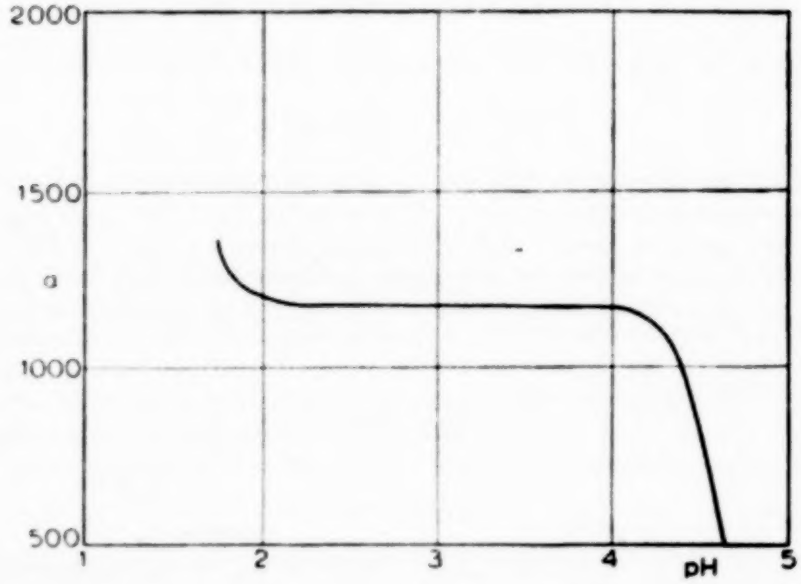

Fig. 3. Absorbance index (400 mμ) of silicomolybdic acid as a function of pH.

Even large amounts of neutral salts do not affect the absorbance values appreciably, but elements reacting like silicon may produce a yellow color. We have investigated the influence of phosphorus, arsenic and germanium. The absorbance index of phosphorus is plotted in Fig. 1.

The most interfering of these elements is phosphorus, and therefore a large number of masking agents were tried: oxalic acid, tartaric acid, citric acid, lactic acid, phthalic acid, ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA) and others. The best results were obtained with tartaric acid, but even then the phosphorus color was not completely masked, and also the color of the silicomolybdic acid faded slightly when this reagent was used. This fading was less when the tartaric acid was added after the silicomolybdic color had completely developed. As our samples usually contained very small amounts of phosphorus, we preferred not to use a masking agent but to apply a correction to the result. At 390 mμ the absorbance of one part of P_2O_5 corresponds to that of 0.43 part of SiO_2. For germanium the relationship is about the same, but the absorbance is very sensitive for small variations in pH. The absorbance due to arsenic can usually be neglected as one part of As_2O_5 corresponds to less than 0.01 part of SiO_2.

In dissolving silicate melts the formation of precipitates can be more or less completely avoided by the addition of EDTA. Since EDTA forms complex compounds with molybdenum, the influence of EDTA on the determination of silicon was investigated. Experiments showed that EDTA does not affect the results if the concentration of EDTA in the sample solution is less than 0.01*M*.

Rocks and other silicate materials often contain relatively large amounts of iron. The iron-EDTA complex formed when EDTA is present has an appreciable absorbance at the wave-length used, as can be seen in Fig. 1. The best way of eliminating this interference is to measure the absorbance of the unknown solution not against water but against a sample of the unknown solution to which no ammonium molybdate has been added.

THE ANALYSIS OF SILICATES

In analyzing insoluble silicates the procedure given below was followed.

Procedure

A suitable amount of the sample, usually 100–300 mg containing 20–70% SiO_2, is weighed and transferred to a nickel crucible containing 10 g of molten NaOH. After 5–10 minutes of heating the melt is cooled and dissolved in a plastic disk containing water and 40 ml of 0.05*M* EDTA (as the disodium salt). The solution is transferred to a tared plastic flask and diluted on a balance until the weight is 509.4 g, *i.e.* 500.0 ml at 20°. Some suitable aliquot of the solution (10–25 ml) is pipetted

TABLE I

Sample	*% SiO_2*	
	theoretical	*found*
Plastic clay No. 98, 0.08% P_2O_5	59.11	58.99
	average value of 8 analyses of	59.19
	Bureau of Standards	59.09
		59.17
Soda lime glass No. 80, 0.08% As_2O_5	73.98	74.10
	average value of 13 analyses of B. of S.	74.24
		74.08
Argillaceous limestone No. 1 A	14.11	14.26
0.15% P_2O_5	average value of 11 analyses of B. of S.	14.26
Standard sample 177 of Portland cement	21.90	22.17
0.05% P_2O_5	analysis of B. of S.	22.09
		22.20
		22.19
		22.13

The theoretical values are average values of analyses reported by U.S. National Bureau of Standards, Washington, D.C. The agreement is satisfactory.

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into a 50-ml volumetric flask containing 10 ml of a suitable mixture of $2M$ monochloracetic acid and $2M$ ammonium monochloracetate and 10 ml of an ammonium molybdate solution containing 0.2 mole Mo per l (35.3 g $(NH_4)_6Mo_7O_{24}\cdot 4\ H_2O$/l). The composition of the buffer solution depends on how much of the alkaline (approx. $0.5M$) sample solution is used. The pH of the solution obtained must be between 3.0 and 3.7. The flask is immersed in boiling water and kept there for 5 to 10 min. The solution is then cooled to room temperature and diluted to 50 ml. The absorbance of the solution is measured at a wave-length of 390 mμ. The 100% transmittance value is adjusted using a solution prepared in the same way but omitting the addition of the ammonium molybdate solution and the heating.

The absorbance is corrected to 20° using the expression $\Delta A = (20-t)\ 0.004A$. The correction is thus negative for temperatures over 20° and positive for temperatures below 20°.

All solutions are prepared using redistilled water free from silica and kept in plastic bottles. The purity of the reagents is checked by a blank determination.

If a Beckman spectrophotometer (or any other one-cell instrument with a 1:10 sensitivity adjustment) is used, it is advantageous to choose the wave-length and silica concentration so that the absorbance is a little above 1.0. A higher sensitivity can then be used, *i.e.* one scale unit of the transmittance scale corresponds to a relative error of about 0.4%[5]. As the reproducibility of a measurement is usually about half a scale unit, the error in analyzing silicate rocks is, as a rule, about ± 0.1% SiO_2.

The absorbance index was determined according to the procedure given above using a solution of pure SiO_2 in NaOH, but since the absorbance curve is rather steep (Fig. 1), the value obtained may depend somewhat on the instrument used. We have used a value $a_{390} = 1.701\cdot 10^3$ (20°). It is advisable to adjust the wave-length very carefully using a magnifying glass. A Beckman DU spectrophotometer was used.

The colors were stable for nearly two days.

The results of some analyses of silicates are given in Table I.

ACKNOWLEDGEMENT

This investigation has been supported by grants from Statens Naturvetenskapliga Kommission, Finland.

SUMMARY

A photometric method for the determination of silicon based on the yellow color of α-silicomolybdic acid is described. The pH must be kept within the range 3.0–3.7, and the equilibrium state is established by heating the solution. Since the color of this modification is remarkably stable and reproducible, a high degree of precision can be attained.

RÉSUMÉ

Une méthode photométrique est proposée pour le dosage du silicium; elle est basée sur la coloration jaune de l'acide α-silicomolybdique. Cette coloration est très stable et reproductible et permet d'obtenir une très bonne précision.

ZUSAMMENFASSUNG

Es wird eine photometrische Methode zur Bestimmung von Silizium beschrieben, die auf der gelben Farbe der α-Silikomolybdänsäure beruht. Wegen der hohen Stabilität und guten Reproduzierbarkeit des Farbtons ist eine grosse Genauigkeit erreichbar.

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DROP-SCALE CHRONOPOTENTIOMETRY

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In recent times the analytical chemist has been confronted more and more with the analysis of trace amounts of substances. In many cases in which the concentrations of the components of mixtures are very small, the materials are first concentrated by evaporation, electrolysis, or other techniques. Even then, the ultimate concentration attainable is quite often too low for most analytical methods unless the volume is decreased to the size of a drop, a volume too small for most analytical techniques. Also it is not uncommon to start with only a drop or two of sample for analysis. SCHREIBER AND COOKE[1] recently described coulometric generation of titrant within a drop of solution. A physico-chemical method of great promise is chronopotentiometry. REILLEY, EVERETT AND JOHNS[2] have published an excellent experimental evaluation of this technique. They pointed out the successful analytical determination of electroactive substances in solutions as dilute as $5 \cdot 10^{-5} M$. The very nature of the technique makes it ideally suited for carrying out analysis on one drop (0.05 ml or less) of solution. This paper describes the application of rapid chronopotentiometry to single drops of dilute solutions of iodide, ferrocyanide, ferricyanide, and zinc ions. In the light of the excellent papers on chronopotentiometry, both theoretical and practical[2-5], that phase of the subject will not be discussed.

EXPERIMENTAL

Reagents

Reagent-grade chemicals were used throughout this investigation. Stock solutions of ferricyanide, ferrocyanide, iodide, and zinc ions were prepared by dissolving known amounts of potassium ferricyanide, potassium ferrocyanide, potassium iodide, and zinc nitrate to known volumes. In the cases of potassium ferrocyanide and potassium iodide solutions, dilutions of the stock solutions were made with deaerated dilute sulfuric acid. The solutions of ferricyanide and ferrocyanide were $0.05 M$ in sulfuric acid. The potassium iodide solutions were $0.08 M$ in sulfuric acid, and the zinc nitrate solutions were $0.1 M$ in potassium nitrate. Sodium sulfite was added to the zinc nitrate solutions to rid the solutions of oxygen. Deaeration of the solutions with purified nitrogen was not satisfactory, due to the rapid absorption of oxygen on exposure to air. Upon electrolyzing deaerated solutions, there was a noticeable interval before the potential of the mercury pool attained that for the reduction of zinc. Such was not the case, however, when sodium sulfite was used to purge the solutions of oxygen.

Apparatus

The chronopotentiometric assemblies used in this experiment are shown in Fig. 1. The reference electrode and auxiliary electrode units in both assemblies were the same. The reference electrode was a Beckman Fiber Type 270 (supplied with the Model G pH meter). A platinum wire wound around the tip of the reference served as the auxiliary electrode. The working electrodes were platinum and mercury. The platinum electrode was prepared by placing a 1/4-inch diameter, stiff paper disc on a 1.5 × 2.5 cm piece of heavy platinum foil and spraying lightly with Krylon (Krylon, Inc., Norristown, Pa.). On drying, a light coating of plastic was left on the surface of the platinum foil except for the area covered by the disc.

The mercury working electrode unit consisted of a 2-inch length of heavy capillary glass tubing (0.25 cm I.D. and 0.9 cm O.D.) with a rubber tubing connected to one end. The top and inside of the capillary were coated with Desicote (Beckman Instruments Inc., South Pasadena, Calif.).

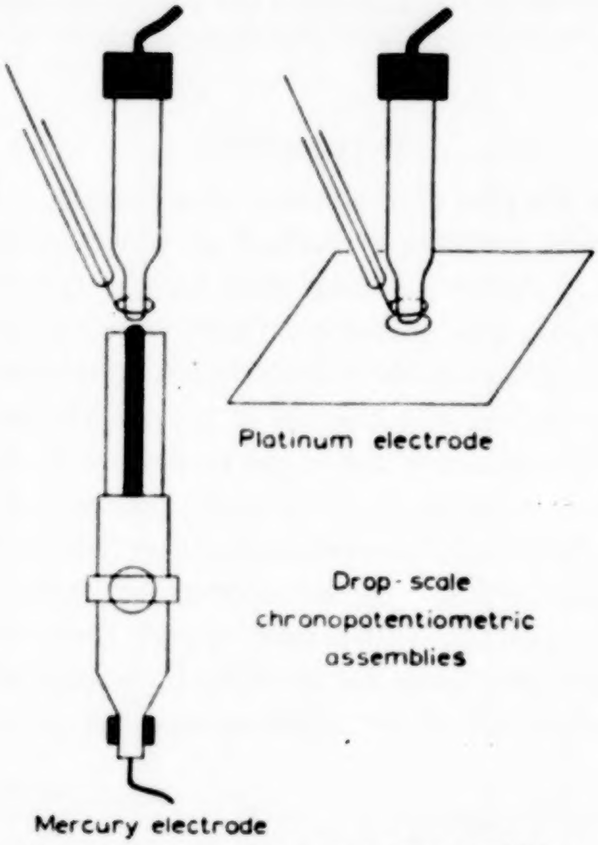

Fig. 1. Chronopotentiometric assemblies.

The end of the rubber tubing was clamped and the capillary and tubing were filled with mercury. The screw clamp attached between the capillary tubing and the clamp at the bottom was used to squeeze mercury out of the capillary to renew the mercury working electrode.

The constant current source was a bank of 45-V "B" batteries connected in series with a megohm resistor (1 to 22 megohms) and a three-way switch. When not being passed through the cell, the current was directed back to the batteries *via* a potentiometer whose resistance was adjusted to match that of the cell. Also in series with the dropping resistor and the batteries was a precision resistor (1% tolerance). The electrolysis current was determined by measuring the potential drop across the resistor with a Beckman Model G pH meter. The values of the precision resistors were sufficient for current measurements good to 1%.

The potential of the working electrode *versus* the reference S.C.E. was fed into a Leeds and Northrup pH Indicator whose output was recorded on a Varian Model G-10 Graphic recorder at a chart speed of 8 inches/min.

The potential of the working electrode *versus* the reference S.C.E. was also fed into a Sargent Malmstadt Automatic Titrator which actuated a timer through a relay. The potential change, however, was so small and gradual that the biasing voltage at the grid of the first thyratron tube in the Titrator had to be reduced to such a value that very erratic times were obtained. A three-electrode differential derivative technique was also studied. Here the potential difference between two working electrodes operating at different current densities was followed by the Titrator[6].

Procedure

1–2 drops (0.05–0.10 ml) of solution were placed on the platinum foil or the top of the capillary tube such that the uncoated section of the platinum foil or the mercury surface was completely covered. The reference electrode and the auxiliary electrode unit was then moved over and on top of the drop. The recorder was started and the solution was electrolyzed. After the chronopotentiogram was obtained, the electrode unit was moved aside and the platinum electrode and the reference electrode and auxiliary electrode unit were washed and blotted dry with filter paper. In the case of the mercury electrode, special care was taken to dry the capillary. The mercury electrode was renewed by tightening the screw clamp. Excess mercury was removed by running the edge of a filter paper across the top of the capillary.

Aside from the time involved in the electrolysis period, which never was longer than one minute, each run took only about one minute.

The same procedure was followed in the derivative studies with the Sargent Malmstadt Automatic Titrator. In the three-electrode differential derivative technique, the reference electrode was replaced with a small button-type platinum electrode, which served as a common auxiliary electrode.

PERFORMANCE

Figs. 2, 3 and 4 show the plot of $\tau^{1/2}$ *versus* concentration for the oxidation of ferrocyanide and iodide ions and the reduction of ferricyanide ions at the platinum working electrode. Fig. 5 shows a similar plot for the reduction of zinc ions at the mercury working electrode. The transition times were evaluated from conventional chronopotentiograms. In all cases, the curves do not pass through the origin, but cross the abscissa. In the case of zinc at a current of 3.3 μA, the curve (not shown) crossed the ordinate. The discrepancy is not due to the technique used in evaluating transition times, as several different methods gave virtually the same point of intersection. The important linear relationship of $\tau^{1/2}$ *versus* concentration, however, held in all cases.

Each point in the plots represents the average of four to six runs. The average deviation for each point was 1%. In the case of zinc, however, the average deviation was 2 to 6%. The large deviation was due to difficulty in reproducing the electrode area. When mercury is squeezed out of the capillary and the excess scraped off with the

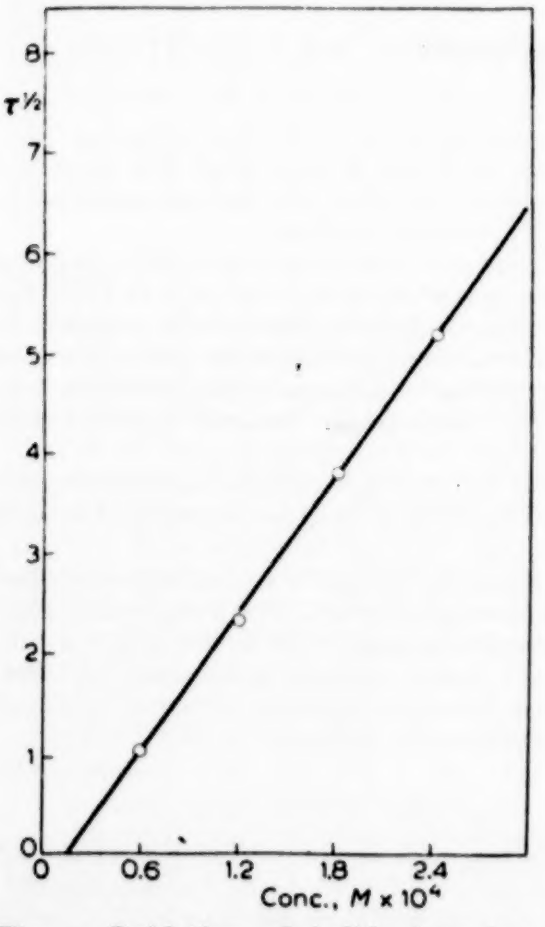

Fig. 2. Oxidation of iodide ions in 0.08M sulfuric acid at 6.8 μA.

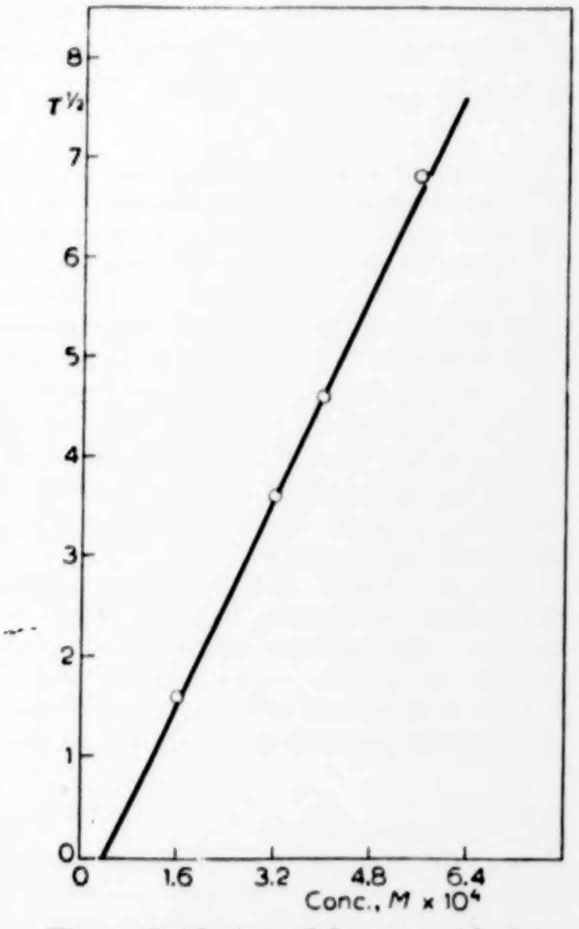

Fig. 3. Oxidation of ferrocyanide ions in 0.05M sulfuric acid at 6.4 μA.

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edge of a filter paper, the mercury level could be slightly below or above the top of the capillary. The area in the latter case would be larger than in the former.

Fig. 6 shows the potential-time plots for the oxidation of iodide ions in $5 \cdot 10^{-6} M$ potassium iodide solution at 1.1 μA (A) and the background scan (B) obtained on 0.07 ml of solution. A potential holdup is clearly indicated for the oxidation of iodide ions. The amount of iodide ions in the drop was $3.5 \cdot 10^{-10}$ equivalents. The detection of much smaller amounts of electroactive substances is complicated by the foot of the decomposition wave of the supporting electrolyte solution being magnified with decreasing current densities. In chronopotentiometry, the detectable limit is not simply determined by the background scan as is the case in polarography.

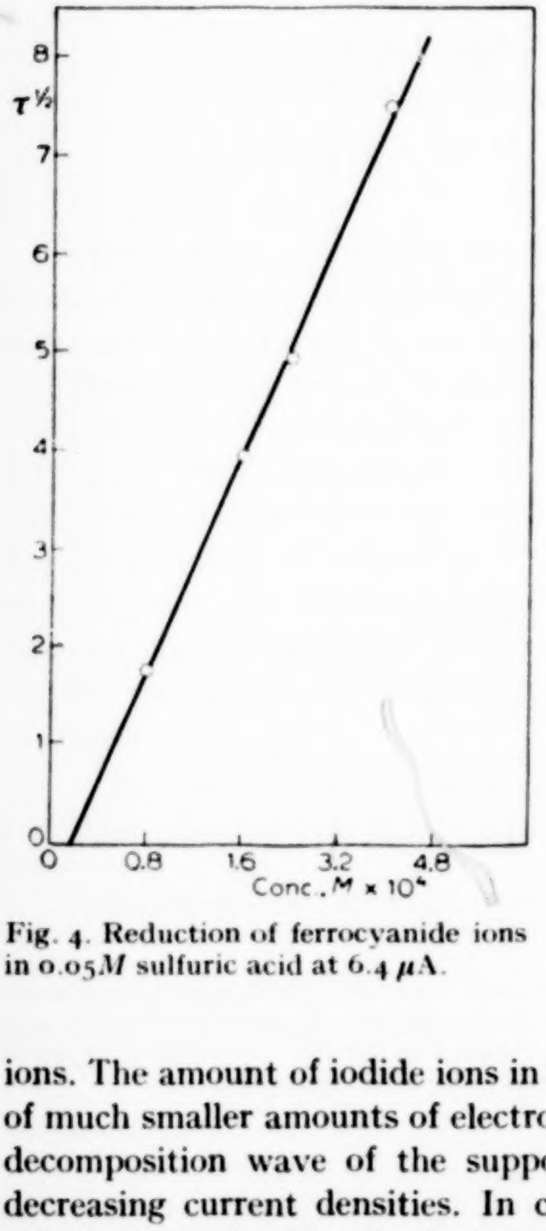

Fig. 4. Reduction of ferrocyanide ions in 0.05M sulfuric acid at 6.4 μA.

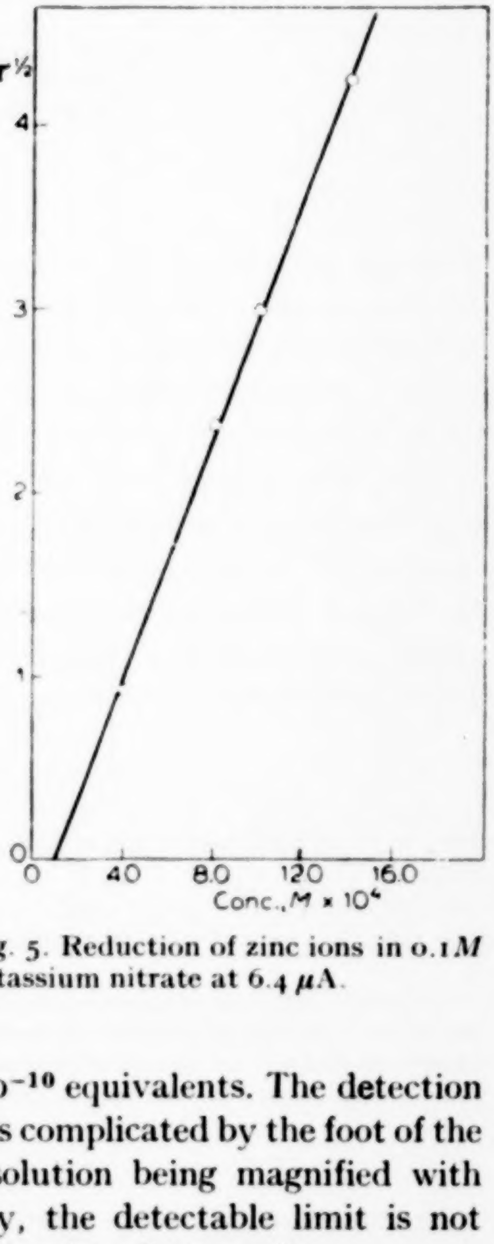

Fig. 5. Reduction of zinc ions in 0.1M potassium nitrate at 6.4 μA.

Transition times for the reduction of ferricyanide ions were also obtained by two derivative techniques. In one, the potential between the working electrode and the reference electrode was followed with the Sargent Malmstadt Automatic Titrator which fed a derivative of the potential into a recorder. In the other, a differential technique was used. The potential difference between two working electrodes operating at different current densities was followed by the Titrator, which fed the derivative of the potential difference into a recorder. Although both types of derivative chronopotentiograms, when evaluated, gave the same transition time as the conventional chronopotentiogram, the derivative signals of the differential technique were much sharper.

Use of the Titrator to turn off a timer by either of the two techniques was unsuccessful for the concentration range investigated due to the lack of sharp potential changes from one electrode process to the next. Decreasing the bias voltage resulted in the Titrator firing prematurely. Increasing the bias voltage to prevent premature firing invariably resulted in the Titrator not firing at all.

Obviously, much smaller volumes of solution can be handled by this technique by decreasing the area of the electrode. The reference electrode can be ground to a finer point so as to enable it to be placed in smaller volumes of solution.

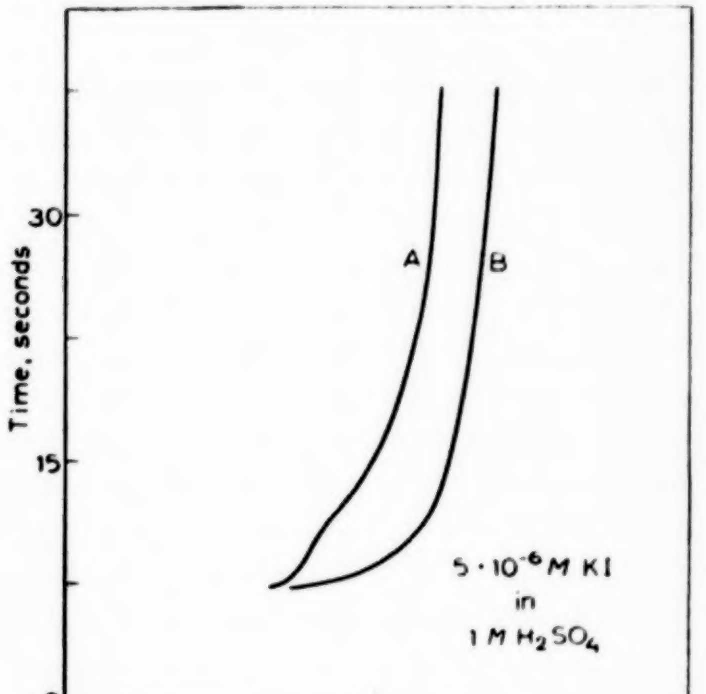

Fig. 6. Potential–time curves for the oxidation of iodide ions (A) and the supporting electrolyte solution (B). Current 1.1 μA.

SUMMARY

Chronopotentiometry has been successfully carried out on one drop of solution. A simple arrangement enabled determinations to be performed in one to two minutes. A potential holdup was clearly indicated for the oxidation of iodide ions on electrolyzing 0.07 ml of a $5 \cdot 10^{-6} M$ potassium iodide solution $1 M$ in sulfuric acid, a total of $3.5 \cdot 10^{-10}$ equivalents of iodide ions.

RÉSUMÉ

La chronopotentiométrie a été effectuée avec succès sur une goutte de solution. Un dispositif simple permet de faire des dosages en une à deux minutes.

ZUSAMMENFASSUNG

Chronopotentiometrische Messungen sind mit Erfolg bei einem Tropfen Lösung angewandt worden. Dauer einer Bestimmung: 1–2 Minuten.

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POLAROGRAPHIC REDUCTION OF HEXAVALENT URANIUM IN SODIUM TRIPOLYPHOSPHATE

I. GENERAL STUDIES

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FRANKENTHAL AND NEUBERG[1] were the first to report on the interesting masking effects of sodium tripolyphosphate. FEIGL[2] later observed that this reagent was far more effective in masking inorganic precipitations than any known at the time. Yet tripolyphosphate has not found many applications in analytical chemistry.

JANKOVITS[3] has recently used sodium tripolyphosphate in a manner similar to EDTA for the direct titration of calcium and magnesium. VAN WAZER AND CAMPANELLA[4] have shown that the condensed phosphates shift the half-wave potentials of barium and even of sodium by complex formation. An understanding of the polarographic behaviour of the tripolyphosphate complexes may lead to useful analytical applications, but literature on the subject is meagre. This paper describes some observations on the polarographic reduction of the tripolyphosphate complex of hexavalent uranium.

EXPERIMENTAL*

Reagents

All the reagents used were tested and found to be polarographically pure. The sodium tripolyphosphate was an anhydrous, granular material supplied on request by Blockson Chemical Co., Inc.

Standard uranyl sulphate was prepared by fuming uranyl nitrate with sulphuric acid to a paste, dissolving in water and making up to volume. Its uranyl content was estimated by reduction through Jones' reductor followed by titration with ceric solution.

Apparatus

(1) Tinsley Recording Polarograph.

(2) Doran glass electrode pH meter.

(3) Polarographic cell. An H-type cell carrying an S.C.E. as reference electrode. An agar bridge (4% agar saturated with potassium chloride) reinforced by a coarse-porosity sintered pyrex disc was used in the cross-member. The cell resistance was about 500 ohms.

Procedure

Polarograms were taken at 30.0 ± 0.1° unless otherwise stated. Oxygen was removed from the test solution by bubbling purified nitrogen for fifteen minutes. The capillary had an m value of 1.68 mg/sec, and the mean drop-time was 4.204 sec/drop at a potential of -1.3 V and h 36 cm.

Mixtures of penta- and hexa-valent uranium for the composite polarograms were prepared by controlled potential electrolysis[5] of a 2 mM uranyl perchlorate solution in 0.1 M sodium perchlorate. The pH was maintained at 2.7 and the cathode potential at -0.55 V *vs.* Ag/AgCl electrode. Electrolysis was carried out for 45 minutes in an atmosphere of nitrogen.

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* Abbreviations used in the text: UTP, uranyl tripolyphosphate complex; NaTP, sodium tripolyphosphate; h, mercury pressure corrected for back pressure; S.C.E., $E^1/_2$, id, i, m and t have their conventional significance.

RESULTS

Reduction of some common radicals in presence of NaTP

The $E^{1}/_{2}$ for the radicals examined are listed in Table I. Cr^{+3}, Co^{+2}, Ni^{+2}, Zn^{+2}, Ti^{+4}, WO_4^{-2}, MoO_4^{-2}, Sn^{+4}, Mn^{+2} gave no steps in the available potential range. Ceric cerium gave a drawn-out wave. Copper gave two waves, the height of the first wave being considerably less than that of the second. No waves except the first one for copper showed an apparent maximum.

The rest of the present paper deals exclusively with the polarographic behaviour of uranyl tripolyphosphate complex.

TABLE I

REDUCTION OF TRIPOLYPHOSPHATE COMPLEXES

Electrolyte composition: 1 m*M* depolarizer under test, 0.1*M* NaTP, 0.1*M* KCl, 0.02*M* borate buffer, pH 9. KCl replaced by K_2SO_4 in the case of ceric ion.

Depolarizer	*$E^{1}/_{2}$ vs. S.C.E. in V*	*Voltage span in V*	*Remarks*
—	—	—	Current rise at —1.81 V
Bi^{+3}	—0.53	—0.4 to —0.7	Well-developed wave
Pb^{+2}	—0.66	—0.6 to —0.75	Very well-developed
Fe^{+3}	—0.76	—0.55 to —0.95	Drawn-out wave
Cu^{+2}	—0.25	—0.2 to —0.35	Rounded maxima
	—1.18	—0.9 to —1.5	Drawn-out
VO_3^-	—1.32	—1.1 to —1.5	Well-developed
AsO_3^{-3}	—	—	Discharge at —1.4
Ce^{+4}	—	—0.8 to —1.5	Ill-defined, and drawn-out
Cd^{+2}	—1.2	—0.75 to —1.55	Appears to consist of two overlapping waves
UO_2^{+2}	—1.07	—0.8 to —1.25	Well-developed

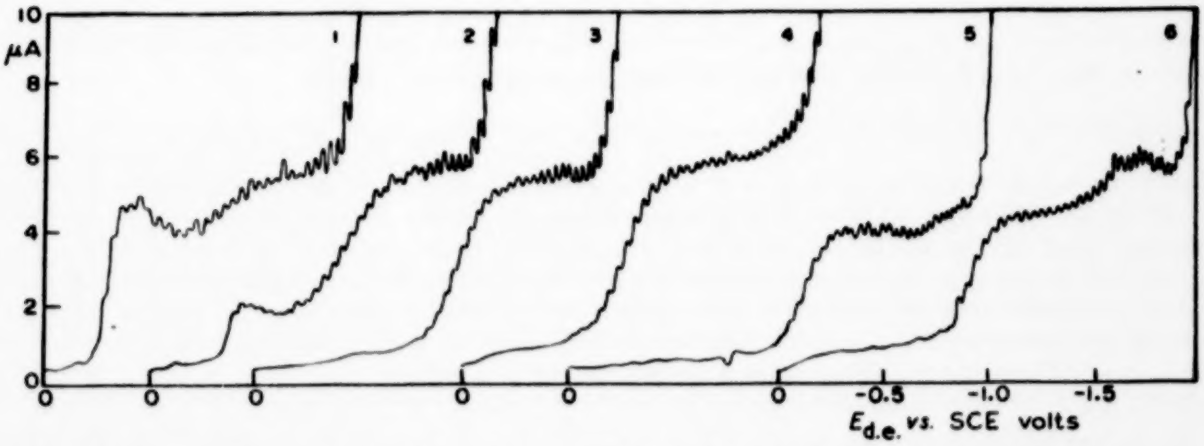

Fig. 1. Polarogram of 1 m*M* uranyl ion in 0.02*M* $Na_5P_3O_{10}$, 0.2*M* KCl and adjusted to: 1–pH 3; 2–pH 4; 3–pH 5; 5–pH 9; 4 and 6 were at pH 5 and pH 9 respectively but contained 1*M* KCl.

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Effect of pH

The polarograms of unbuffered solutions at different pH are recorded in Fig. 1. Both *id* as well as $E^1/_2$ change with pH (Table II). Buffered solutions behaved similarly except for a solution buffered to pH 5 with phthalate, in which case the polarogram appeared to consist of two waves, the first starting around —0.4 V and merging with the second at —0.7 V.

TABLE II (*cf.* Fig. 1)

EFFECT OF pH ON UTP WAVE

pH	*$E^1/_2$ vs. S.C.E.*	*id (μA)*
3	—0.86 [a]	1.0 [a]
4	—0.92 [a]	3.8 [a]
5	—1.00	4.5
9	—1.10	3.2

[a] Refers to the second wave corresponding to reduction of UTP.

Effect of variables on id

The temperature coefficient of *id* as measured between 30° and 40° were 1.7% and 1.0% per degree at pH 9 and pH 5 respectively. Any change in $E^1/_2$ between these temperatures was not appreciable. The effect of mercury pressure on the diffusion plateau is indicated in Fig. 2. The values for $id/\sqrt{h}$ at pH 9 and pH 5 are shown in Table III. The diffusion current constants at 30°, as obtained from the linear plot of *id vs. c* (Fig. 3), were 2.44 and 1.65 at pH 5 and pH 9 respectively. There was no noticeable change in $E^1/_2$ with change in uranyl ion concentration (0.1–5 m*M*) or with change in the concentration of NaTP (0.01*M*–0.2*M*).

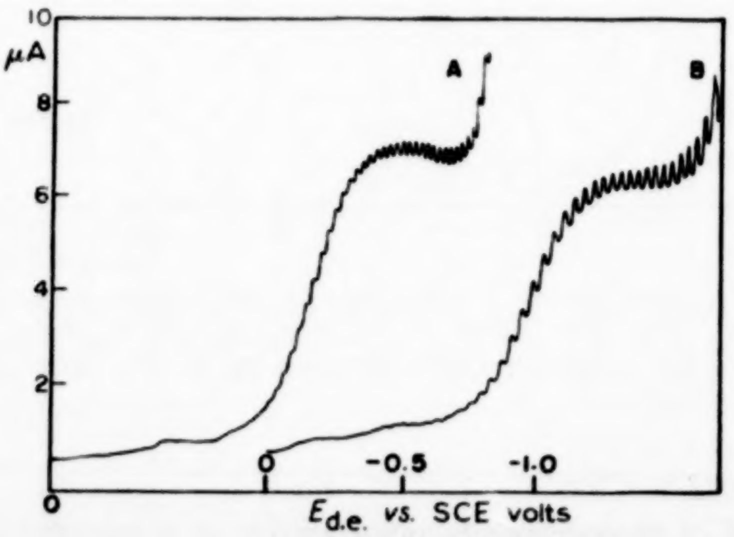

Fig. 2. Polarogram of 1 m*M* uranyl ion in 0.5*M* $Na_5P_3O_{10}$ and 0.1*M* KCl, pH 9. A – Hg ht. 49 cm; B – Hg ht. 36 cm.

TABLE III

UTP WAVE, *id vs. h*

pH 9		*pH 5*	
Mercury pressure (cm)	*id/$\sqrt{h}$*	*Mercury pressure (cm)*	*id/$\sqrt{h}$*
34.5	5.19	36	4.25
47.5	5.22	49	4.43
62.5	5.06	64	4.63

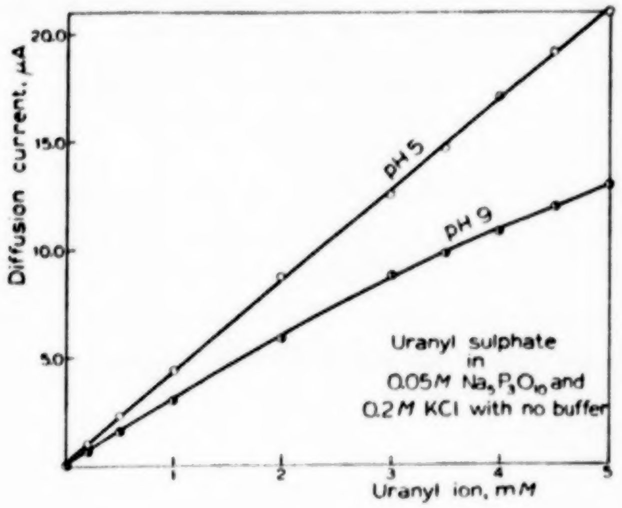

Fig. 3. Diffusion current *vs.* uranyl concentration at 30°.

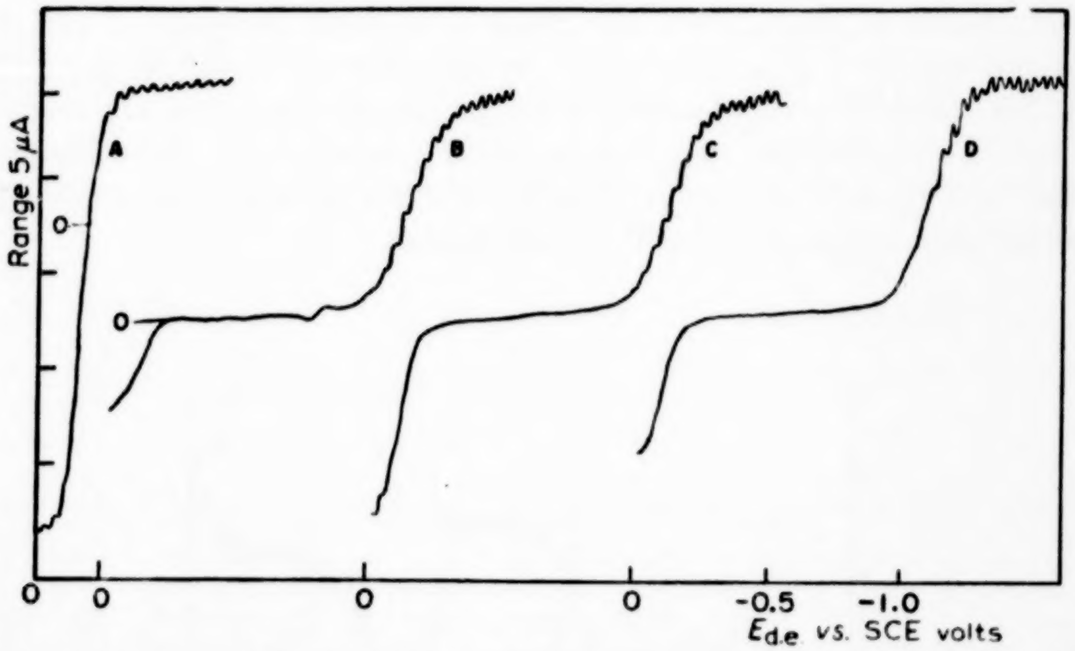

Fig. 4. Composite polarograms of $U^{+5} + U^{+6}$ in sodium tripolyphosphate. A – Uncomplexed $U^{+5} + U^{+6}$, U = 2 m*M*, pH 2.5; B – $U^{+5} + U^{+6}$, (U = 1 m*M*) in 0.05*M* $Na_5P_3O_{10}$, pH 8.4; C – Electrolytically pre-reduced uranyl tripolyphosphate complex pH 9; D – Same as C after standing for 90 min without contact with air.

Composite polarograms of UTP

Fig. 4 is a record of the composite polarograms of a mixture of pentavalent and hexavalent uranium under the following conditions:

A. Perchlorate solution, pH 2.5, uranium 2 m*M*.

B. 1:1 (by vol.) mixture of solution A and 0.1*M* NaTP, final pH 8.43.

C. A UTP solution (2 m*M* uranyl perchlorate in 0.2*M* $KClO_4$ + equal volume 0.1*M* NaTP) electrolysed at pH 9 for 30 min under nitrogen at cathode potential —1.25 V *vs.* Ag/AgCl.

D. Solution C after being allowed to stand under nitrogen in the polarographic cell for 90 min.

Influence of indifferent electrolytes

When the electrolyte concentration is increased by the addition of salts including those which are not known to form complexes with the uranyl ion, the $E^1/_2$ was found to shift in all cases to more positive potentials. This effect is shown in Table IV (*cf.* Fig. 1).

TABLE IV

EFFECT OF INDIFFERENT ELECTROLYTES ON UTP WAVE

Electrolyte composition: 1 m*M* uranyl ion, 0.04*M* NaTP, indifferent electrolyte, pH 9, *h* = 51 cm.

Indifferent electrolyte	$E^1/_2$ *vs. S.C.E.*	*id* (μA)
Nil	—1.27	2.8
0.1*M* KCl	—1.15	3.6
0.6*M* KCl	—0.98	3.2
1.1*M* KCl	—0.92	3.0
1.6*M* KCl	—0.89	2.8
2.6*M* KCl	—0.86	2.8
0.1*M* $NaNO_3$	—1.20	3.0
1.0*M* $NaNO_3$	—1.02	2.8
0.1*M* $NaClO_4$	—1.20	3.1
1.0*M* $NaClO_4$	—1.02	3.0
0.1*M* K_2SO_4	—1.17	3.2
1.0*M* K_2SO_4	—0.97	2.9

Effect of capillary-active substances

Polarograms in presence of some common surface-active agents are recorded in Fig. 5. Their effect on *id* and $E^1/_2$ are listed in Table V.

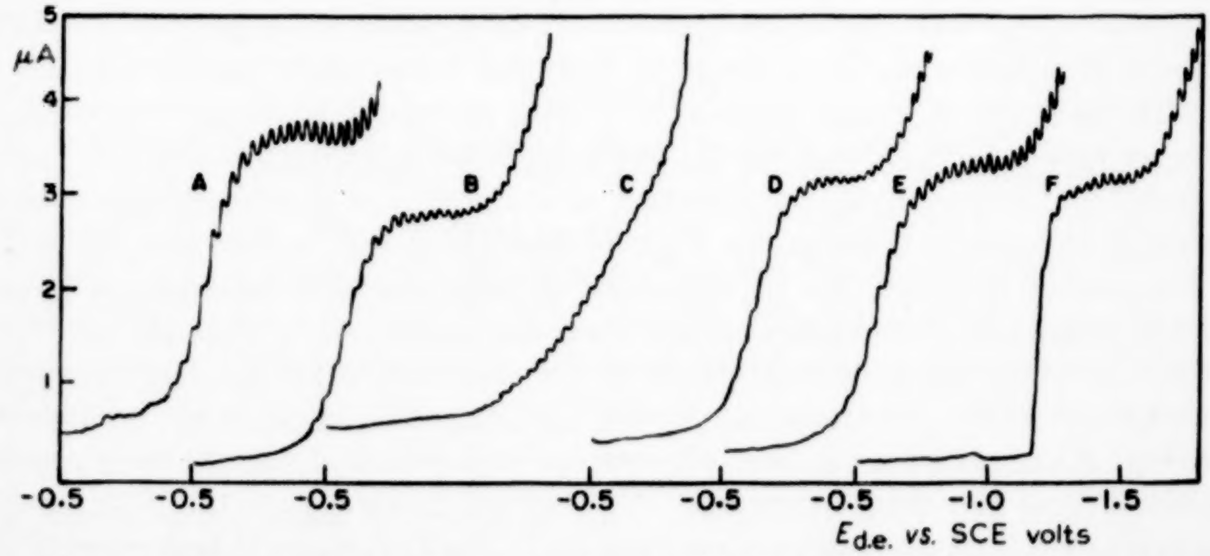

Fig. 5. Polarograms at pH 9 of 0.8 m*M* uranyl ion in 0.05*M* $Na_5P_3O_{10}$, 0.1 *M* KCl, and A – no maximum suppressor, B – 0.001% gelatine, C – 0.01% gelatine, D – 0.01% gum arabic, E – 0.001% camphor, F – 0.01% camphor.

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TABLE V

EFFECT OF MAXIMUM SUPPRESSORS ON UTP WAVE (*cf.* Fig. 5)

Electrolyte composition: 1 mM uranyl, 0.05M NaTP, 0.1M KCl, pH 9, mercury height (h) = 51 cm.

Maximum suppressor (%)	*id* (μA)	$E^1/_2$ *vs. S.C.E.*
Nil	2.9	—1.06
Gelatine		
0.001	2.5	—1.07
0.01 [a]	—	—
Gum arabic		
0.01	2.6	—1.12
0.10	2.5	—1.24
Camphor		
0.001	2.9	—1.08
0.01	2.8	—1.19
0.10	2.3	—1.42

[a] Wave badly deformed.

DISCUSSION

The polarogram of uranyl tripolyphosphate complex (UTP) shows a slight dip near the end of the diffusion current plateau. The dip becomes less pronounced at lower pH, longer drop-times (Fig. 2) and higher concentrations of indifferent electrolytes (Fig. 1). The departure from diffusion control is not considerable[6], as indicated by the normal temperature coefficient, the linear plot of *id vs. c* (Fig. 3), and the fairly constant value for $id/\sqrt{h}$ (Table III).

The irreversible nature of the wave is apparent from its large voltage span and the resulting high reciprocal slope (0.115 V at pH 9) of the plot E *vs.* log $i/(id - i)$. For this reason, the formula and the dissociation constant of the uranyl tripolyphosphate complex could not be determined polarographically.

The uranyl ion in presence of NaTP gives two waves in the pH range 3-4 (Fig. 1). The first wave with $E^1/_2$ around —0.3 V (Table II) is, in all probability, caused by the reduction of uncomplexed uranyl ion. Its disappearance seems to indicate that complexation of uranyl with NaTP is complete above pH 5. Greater stability of the complex in neutral to alkaline media is apparent from the increasingly negative values for $E^1/_2$ with rising pH. A steady decrease in *id* with increasing pH is also observed, the reason for which is not clear. A similar observation has been reported by SENISE AND DELAHAY[8] on the polarographic reduction of thallium in a pyrophosphate medium.

From the composite polarograms Figs. 4A and 4B, it will be seen that the anodic portions, caused in either case by the oxidation of pentavalent uranium, differ considerably from each other in their $E^1/_2$ values. The anodic wave (Fig. 4B) at $E^1/_2$ = approx. —0.1 very probably corresponds to the oxidation of pentavalent uranium in the complexed state. An anodic wave with the same $E^1/_2$ is given by a solution of UTP (Fig. 4C) provided it has been pre-reduced at a potential slightly more negative than the $E^1/_2$ of the uranyl complex. It, therefore, appears that the polarographic reduction of UTP complex proceeds essentially to the U^{+5} stage. Whether any U^{+4} is also formed in the process is difficult to say, since U^{+4} in presence of NaTP did not give an anodic wave.

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The marked shift in the $E^1/_2$ to more positive values (Table IV) with increasing concentration of an indifferent electrolyte seems too high to be caused entirely by increased ionic strength. ORLEMANN AND KOLTHOFF[9] and, later, DELAHAY AND MATTAX[10] noted similar behaviour in the irreversible reductions of iodate and bromate. To explain the positive shift, the latter authors postulated the formation of a transitory collision complex between the cation and the iodate ion. The cation which functions as a bridge between the reducible anion and the cathode facilitates electron transfer.

Maximum suppressors shift $E^1/_2$, particularly of irreversible waves, to more negative potentials[7]. The effect of some of them on the UTP wave is set out in Table V (*cf.* Fig. 5). Gum arabic has a perceptible though not a pronounced effect, while gelatine in as low a concentration as 0.01% almost obliterates the wave. The gelatine effect resembles that observed by MEITES[11] on the polarogram of copper in alkaline tartrate medium. With camphor, however, the current rises abruptly, rendering the wave very steep[12,13]. When the solution is almost saturated with camphor (0.1%), the UTP wave starts only at —1.4 V which is nearly the desorption potential [12] of camphor. With a moderate concentration of camphor (0.01%), the steepening of the wave is not accompanied by a change in *id*. Advantage may be taken of this fact in the polarographic estimation of uranium.

SUMMARY

The behaviour of some tripolyphosphate complexes at the dropping mercury electrode has been examined, in particular that of the uranyl tripolyphosphate complex. The uranyl ion in alkaline tripolyphosphate medium undergoes an irreversible one-electron reduction with an $E^1/_2$ of —1.07 V *vs.* S.C.E. at pH 9. Indifferent salts shift the $E^1/_2$ to more positive potentials whereas maximum suppressors have an opposite effect. The wave obtained in presence of 0.01% camphor is well-defined and suitable for use in uranium analysis.

RÉSUMÉ

Les auteurs ont étudié le comportement des complexes formés avec le tripolyphosphate de sodium et divers cations, en particulier l'uranium. La vague obtenue en présence de camphre à 0.01% est bien définie et peut servir au dosage de l'uranium.

ZUSAMMENFASSUNG

Es wurde das Verhalten einer Tripolyphosphat-Komplexe, besonders der des Uranyl-Tripolyphosphates, untersucht. In Gegenwart von 0.01% Kampher ist der Verlauf der Kurve so eindeutig, dass die Methode zur Bestimmung des Urans geeignet erscheint.

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ANALYSIS OF SULPHONYL CHLORIDES BY POLAROVOLTRIC TITRATION WITH SODIUM SULPHIDE

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The usual method for analysis of sulphonyl chlorides depends on hydrolysis to hydrochloric acid and the corresponding sulphonic acid which are then titrated. Alternatively, hydrolysis can be carried out with a measured excess of standard alkali and the unused part back-titrated after complete reaction. In many cases, however, complete hydrolysis is slow and in the present work a faster method of analysis has been worked out.

Reaction of sulphonyl chlorides with sodium sulphide

This reaction has been used for many years in the industrial preparation of sulphinates and TRUCE AND MURPHY[1] quote numerous examples in their review. The first reaction is

$$R \cdot SO_2Cl + Na_2S \rightarrow R \cdot SO_2Na + NaCl + S.$$

GILMAN[2] gives a further reaction which takes place at higher temperature

$$R \cdot SO_2Na + S \rightarrow R \cdot SO_2SNa.$$

Although apparently not mentioned in the literature, the first reaction is evidently fast, even in dilute solution, and forms the basis of the titration method described in the present article. Two types of titration of sulphonyl chlorides with sodium sulphide solutions have been carried out:

(1) Visual titration, with the persistence of a yellow colour as end-point. This is evidently caused by the formation of yellow polysulphides between the reaction product sulphur (appearing as an almost colourless suspension) and the excess of the sodium sulphide titrant

$$Na_2S + xS \rightarrow Na_2S_{x+1}.$$

This end-point is arrived at only in more concentrated solutions (0.05–0.1 M).

(2) Polarovoltric titration with the "Titravit" apparatus. The jump in potential taken as end-point is mainly caused by excess of sodium sulphide reagent.

It was observed in practice that the visual and instrumental end-points coincided. Further, in the concentration range studied in this work, end-point and equivalence-point appeared identical at least within the limits of titration error.

EXPERIMENTAL

Sulphonyl chlorides

Those used were:

methane sulphonyl chloride – Eastman Kodak, distilled
benzene sulphonyl chloride – Eastman Kodak, distilled
p-toluene sulphonyl chloride – B.D.H., not less than 98% pure
p-chlorobenzene-, *p*-bromobenzene-, *p*-methoxybenzene- and tetralin -sulphonyl chlorides
benzene *m*-disulphonyl chloride.

All were prepared according to the method of Huntress and Carten[3] and purified by repeated crystallisation from mixtures of petroleum ether, diethyl ether and chloroform. The benzene disulphonyl chloride proved most difficult to purify on account of its low solubility in available solvents.

Solutions

Sodium sulphide (Prolabo pour analyses) 0.5 and 0.1 M in freshly distilled and boiled water (to expel dissolved oxygen as much as possible). The solutions were freshly prepared every few days and standardised with iodine solution just before use.

Sulphonyl chlorides in dry acetone, 0.5 and 0.1 M with factor. These solutions maintained a sensibly constant titre for at least several days.

Apparatus

Commercially available Titravit apparatus. Electrodes each of about 15 mm platinum wire, 0.3 mm diameter, bent into spirals about 5 mm apart from each other.

Procedure

5 ml of sulphonyl chloride solution were measured into a 50 ml beaker, diluted with about 20 ml acetone–water mixture (1 : 1 by volume) and titrated with the sodium sulphide solution under magnetically operated stirring. The visual end-point was the persistence of a distinct yellow colour for 30–60 sec; this was found to be sharp to within a drop of titrating solution (error of less than 1%) in the 0.05–0.1 M range of concentration.

The instrumental titration was carried out on the same quantities by the procedure previously described[4]. To eliminate the gradual change of electrode potential during the earlier part of the titration, which is brought about by the increase in electrolyte concentration from zero at the beginning, about 1 ml of approximately M aqueous sodium chloride solution was added to the sulphonyl chloride solution before titration.

The solvent composition and dilution was also varied.

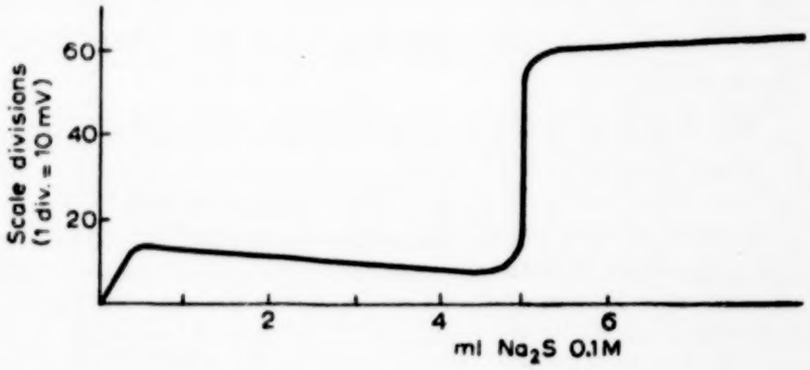

Fig. 1. Titration of 5.0 ml 0.1 M *p*-toluene sulphonyl chloride + 20 ml acetone–water.

RESULTS

Sensitive and stoichiometric titration of all the sulphonyl chlorides was achieved, visually in 0.1 M solution and instrumentally in 0.1 and 0.02 M solution. Fig. 1 shows a typical titration with the Titravit.

The observed potential jumps in 0.1 M solution were of the order of 0.5 V (from +1.6 to about +1.1 V).

The reaction speeds of the various sulphonyl chlorides varied slightly but were in all cases sufficiently high to permit convenient titration.

Under the reaction conditions used, both sulphonyl chloride groups of the benzene *m*-disulphonyl chloride were simultaneously titrated. A rather high result was obtained, probably because the compound contained a small amount of the trisulphonyl chloride. This high result was reduced a little by further recrystallisations.

Effect of different solvent mixtures

Acetone–water mixtures between about 95 : 5 and 40 : 60 (by volume as values at the end of titration) were all found to be equally satisfactory in trials with *p*-toluene sulphonyl chloride. Outside these limits one or other of the reactants was no longer soluble.

Amounts of over about 10% of dioxan led to over-titration with the visual end-point. The yellow polysulphide colour was much less persistent than in absence of dioxan. The polarovoltric end-point was also influenced. The sudden jump of potential was replaced by a series of smaller jumps for several successive dropwise additions of reagent. Up to about 20% dioxan, the middle of the overall potential change corresponded reasonably accurately with the expected titration, so that analysis was still possible, if rather less precise. This disturbing effect of dioxan was observed with all the sulphonyl chlorides studied here. At still higher dioxan concentrations, the interference was too large to permit even an approximate titration. This effect of dioxan has not been examined further in the present work.

Titration at low concentrations

This was not systematically studied, but on the basis of some trials at concentrations of about 0.01–0.005 M, and from consideration of the Titravit titration curves, some forecasts can be made:

(1) A reasonably sharp end-point can be obtained down to about 0.001 M concentration.

(2) In most cases, the speed of reaction should be adequate for titration at concentrations of 0.005 M and in many cases, especially with gentle warming to about 30–40°, for titration of 0.001 M sulphonyl chloride solutions.

(3) End-point and equivalence point should agree satisfactorily at these lower concentrations.

We hope to carry on our studies of these points, and of the kinetics of the reaction.

SUMMARY

A method has been developed for the rapid analysis of aliphatic and aromatic sulphonyl chlorides by polarovoltric titration with a standardised sodium sulphide solution. Visual end-point determination is also possible in more concentrated solution.

RÉSUMÉ

Une méthode est proposée pour l'analyse rapide des chlorures de sulfonyle aliphatiques et aromatiques, par titrage polarovoltrique au moyen d'une solution étalon de sulfure de sodium.

ZUSAMMENFASSUNG

Es wird eine Schnellmethode beschrieben für die Analyse aliphatischer und aromatischer Sulfochloride, welche auf der polaro-voltometrischen Titrierung mit einer Standard-Natriumsulfidlösung beruht.

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REVUES DE LIVRE

Die Methoden der Mikromassanalyse, JOSEF MIKA, Budapest, Zweite umgearbeitete Auflage, xv + 375 Seiten, 76 Abb. und 18 Tab. Geheftet DM 63.—. Ganzleinen DM 66.—. *Die chemische Analyse,* herausgegeben von GERHART JANDER, 42. Band, Ferdinand Enke Verlag, Stuttgart, 1958.

La collection ,,*Die chemische Analyse*'' compte dorénavant dans son actif une des monographies des plus complètes et des plus importantes qu'un microchimiste puisse désirer: ,,*Les méthodes de la microanalyse volumétrique*''.

Le volume que nous avons entre les mains constitue la deuxième édition, entièrement refondue et augmentée, du livre homonyme paru, pour la première fois, en 1939.

Le Professeur MIKA a su, d'une manière admirable, développer le sujet dans toute son ampleur, sans pour cela négliger les détails. Extrêmement systématique et rationel, l'auteur examine successivement les réactifs et instruments utilisés pour les microanalyses volumétriques, les différentes méthodes appliquées actuellement et les causes d'erreur inhérentes à chacune d'elles, la théorie étant partout suivie de nombreux exemples pratiques.

L'érudition et l'expérience personnelle de l'auteur (plus de 600 références bibliographiques) éblouissent littéralement le lecteur et confèrent à cet ouvrage une valeur très grande.

Vu le nombre considérable des sujets traités dans le livre en question, il ne nous est pas possible de donner ici même un bref aperçu des chapitres. Nous relèverons donc au hasard quelques titres: *Allgemeiner Teil:* Die indirekte Bestimmung des Äquivalenzpunktes. Die photometrischen Titrationen. Die potentiometrische Indikation. Die amperometrische Indikation der Mikrotitrationen. Die Mikrotitrationen mit Hochfrequenzindikation. Die Fehlerquellen der volumetrischen bzw. gravimetrischen Bestimmung von Lösungsmengen. Die verschiedenen Arten der Mikrobüretten. Die coulometrischen Mikro- bzw. Ultramikrobestimmungen. Der Wirkungsgehalt der Masslösungen. Die Unterteilung der Probelösungen. Die Mikro- und Ultramikropipetten. *Spezieller Teil:* Neutralisationsanalytische Bestimmung von schwachen Basen in nicht wässrigen Lösungen. Alkalimetrische Bestimmung von Salzen mit Hilfe von Kationenaustauschern. Die Oxydation und Reduktion der Proben. Die wichtigsten Massflüssigkeiten der redoxymetrischen Mikrobestimmungen. Die Komplexbildungstitration. Die fällungsanalytischen Titrationen.

En conclusion, nous tenons à recommander chaudement cet ouvrage à tous les analystes, persuadés qu'il leur sera de toute utilité et leur rendra les services les plus grands.

I. KAPÉTANIDIS (Genève)

Proceedings of the Congress on Modern Analytical Chemistry in Industry, The Society for Analytical Chemistry, W. Heffer & Sons, Ltd., Cambridge, Great Britain, 1958, 244 p., 2 guineas.

Ce livre renferme les exposés présentés lors du Congrès organisé en juin 1957 par ,,The Scottish Section of the Society for Analytical Chemistry''. A la lecture de cet ouvrage, on se rend compte de l'importance que revêt pour l'industrie, la chimie analytique moderne. Elle dispose actuellement de tels moyens d'investigation que son domaine s'élargit sans cesse. Outre les dosages qui deviennent de plus en plus délicats, la chimie analytique a aussi pour objet la recherche des propriétés physico-chimiques des substances, de leur stabilité, des constantes acide – base, ox. – red., etc., connaissances indispensables à la bonne marche et au progrès de l'industrie chimique. C'est ce que nous apprend cet ouvrage. Il est divisé en trois sections, la première s'intitule: ,,L'analyse dans l'industrie moderne'' et comprend entre autres: les recherches analytiques et ses rapports avec l'industrie, les méthodes analytiques modernes dans l'industrie du fer et de l'acier, les problèmes chimiques dans l'industrie électrique, l'application des méthodes physiques d'analyse à l'industrie du gaz, les développements analytiques dans les laboratoires pharmaceutiques. La section II traite de quelques applications des nouvelles techniques analytiques dans l'industrie avec, comme chapitres essentiels: l'analyse et les aliments, les récents progrès dans la séparation des substances à hauts poids moléculaires, la spectroscopie d'émission dans l'analyse industrielle, l'analyse dans la recherche médicale, l'analyse et la spectroscopie infra-rouge. Il est aussi question des plastiques, des métaux rares, de la productivité et de l'automation. La dernière section s'occupe du développement de la chimie analytique et de ses applications à de nouveaux problèmes posés par l'industrie: nouveaux réactifs, utilisation des isotopes radioactifs, mesures analytiques automatiques, polarographie, chromatographie des gaz. Les divers exposés sont clairs, bien présentés, remarquablement documentés. En conclusion: un livre très instructif, à recommander.

D. MONNIER (Genève)

BUCHBESPRECHUNG

Fortschritte der pH-Messtechnik, von KURT SCHWABE, 2., überarbeitete und erweiterte Auflage, VEB Verlag Technik, Berlin, 1958, 280 S., 99 Abb., DM 18.—.

Es ist eine bekannte Tatsache, dass die Anzeigegenauigkeit moderner pH-Messgeräte häufig mit der Messgenauigkeit verwechselt wird. Das Verdienst des Verfassers ist es, auf diesen Umstand und die oft nicht genügend beachtete grundsätzliche Unsicherheit der praktischen pH-Messung in Lösungen unbekannter Zusammensetzung eindringlich hingewiesen zu haben. Das ganze Buch steht unter diesem Aspekt und ist gekennzeichnet durch eine sorgfältige Abschätzung der Messgenauigkeit und Fehlermöglichkeiten, so dass es auch einem Nichtfachmann, der pH-Messungen nur als Mittel zum Zweck durchführt, eine kritische Beurteilung seiner Messwerte ermöglicht.

Der Autor bringt zunächst einen ausgezeichneten Überblick über die verschiedenen Möglichkeiten zur Definition der pH-Skala. Relativ kurz werden dann die nichtelektrometrischen, die katalytischen und kolorimetrischen Methoden zur Bestimmung des pH-Wertes behandelt.

Entsprechend ihrer grossen Bedeutung ist im 3. Kapitel den elektrometrischen pH-Messmethoden der weitaus grösste Teil des Buches gewidmet. Zunächst wird die Wasserstoffelektrode als Grundbezugssystem für die gesamte pH-Messtechnik eingehend besprochen. Dann folgen andere, ebenfalls auf Wasserstoffionen ansprechende Elektroden: die Chinhydronelektrode als wichtigste Redoxelektrode, die Antimon- und Wismutelektrode als wichtigste Metall/Metalloxydelektroden. Besonders ausführlich wird auf die Glaselektrode eingegangen, der wegen ihrer universellen Anwendbarkeit in der praktischen pH-Messung heute wohl die grösste Bedeutung zukommt. Der Abschnitt umfasst Ausführungen über Elektrodenfunktion und Theorie der Glaselektrode, Angreifbarkeit, Temperaturbeständigkeit, elektrischen Widerstand und Polarisierbarkeit, Richtlinien für die Benutzung von Glaselektroden und Elektrodenformen. In einem weiteren Abschnitt werden die Bezugselektroden, insbesondere die Kalomel- und die Silber/Silberchlorid-Elektrode, sowie die Elektrolytschlüssel besprochen.

Erst dann folgt der Abschnitt über Messgeräte für elektrometrische pH-Messungen, unterteilt in Kompensationsinstrumente, stromverbrauchende Anzeigegeräte und elektrostatische Messinstrumente, insbesondere Röhrenvoltmeter. Ein abschliessender Abschnitt ist schliesslich dem Registrieren und Regulieren des pH-Wertes gewidmet.

Gegenüber der 1. Auflage sind Aufbau und Anordnung des Textes nur wenig verändert. Einige inzwischen überholte Tabellen und kleinere Absätze sind fortgefallen. Dafür sind an zahlreichen Stellen Erweiterungen vorgenommen worden, die die Fortschritte der pH-Messtechnik der letzten vier Jahre gebührend berücksichtigen. Wesentlich erweitert wurde der Anhang: Ausser der schon in der ersten Auflage vorhandenen Formelzusammenstellung für elektrometrische pH-Messungen wurden Formeln zur näherungsweisen Berechnung des pH-Wertes aus der Elektrolytkonzentration mit Rechenbeispielen neu aufgenommen. Die Tabellen zur pH-Messung mit Farbindikatoren und insbesondere die der pH-Werte von Puffergemischen wurden in erweiterter Form im Anhang zusammengestellt. Dadurch ist die Übersichtlichkeit sowohl des Textes als auch die der Tabellen verbessert worden. Jedoch sollten in der nächsten Auflage auch die Tabellen mit Hinweisen auf die zugehörigen Textstellen versehen werden.

Das kleine handliche Büchlein gibt trotz seiner Kürze nahezu erschöpfend auf alle Fragen des behandelten Gebietes Auskunft, wobei der Schwerpunkt auf der Behandlung der elektrometrischen Messmethoden liegt. Die Darstellung ist ausserordentlich gründlich und verzettelt sich doch nicht in Einzelheiten. Das Werk kann bestens empfohlen werden.

F. UMLAND (Hannover)

A CRITICAL REVIEW OF THE VOLUMETRIC METHODS FOR THE PLATINUM METALS

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The following review deals with the volumetric methods for the determination of the platinum metals which have been recorded up to January 1958. Undoubtedly some will have escaped the author's attention, particularly where their applications have been integrated within a larger scheme of separation and determination. It is hoped that even these will receive attention during subsequent reviews on methods of separation. In any case there is ample evidence for a marked deficiency of acceptable volumetric methods for most of the platinum metals. Furthermore, one cannot escape the conclusion that a more careful and detailed examination of many of the methods now available, made in the light of the increase in knowledge of the behaviour of acid solutions of the metals, will suggest the elimination of some and improvement in others.

It is a surprising fact that the number of recorded volumetric methods for the determination of the platinum metals is only a small fraction of those presented for gravimetric determinations. Furthermore many of the proposed volumetric methods can be considered useful only when applied to the isolated platinum metal constituent and applied under carefully controlled conditions. The analytical researcher in the field of the platinum metals seems not always to have realized the degree of complexity of the equilibria existing in mineral acid solutions of these metals. This is made evident by the general failure to deal adequately with methods of dissolution prior to the application of the volumetric methods. These, like colorimetric, are sometimes peculiarly sensitive to changes in identity of the dissolved metal constituent. This is particularly true of some of the proposed potentiometric titrations where one may encounter almost totally different valence states in various acid concentrations. Indeed, there are recorded volumetric methods which claim quantitative application in weak acids for one valence, and for a second valence in strong acids. One cannot avoid concern about procedures whose successful application is dependent upon either the enforcement of a practically complete equilibrium through control of acidity, prior oxidation, etc. or upon the development of an equilibrium mixture of constant composition.

Regarding the general status of volumetric methods for the platinum metals there is much to be desired. There is a paucity of acceptable methods for all of these metals and for some no really acceptable method is available.

PALLADIUM

About a dozen methods have been recorded for the volumetric determination of palladium. Many of these involve the formation of insoluble palladium compounds and incorporate some physical process for ascertaining the stoichiometric end-point. Several of the methods require the addition of an accurately measured excess of a standard complexing reagent with the excess determined by a back titration. None of the methods can be applied indiscriminately for the analysis of even simple platinum metals systems. A few of the procedures are useful for routine analysis of simple alloys whose constituents vary little in proportions and identity.

Turbidimetric titrations

Perhaps the first volumetric method for palladium was described by KERSTING[1] who titrated a palladium solution directly with potassium iodide to the disappearance of the brown iodide in the supernatant liquid. Obviously this method can be subject to considerable error. A potentiometric titration of palladium with potassium iodide was used by PSHENITSYN and co-workers[2,3]. When hydroquinone was used initially as a reducing reagent there was no interference from platinum(IV), rhodium(III), and iridium(IV). The interference from quadrivalent platinum could also be avoided by the addition of potassium salt to form potassium hexachloroplatinate[3]. One of the most satisfactory iodide procedures is that proposed by ATKINSON and associates[4-6]. One method[4] involved the treatment of a palladium–ruthenium alloy with hydrochloric acid containing a small amount of nitric acid. Subsequent to dissolution ferrous sulphate solution was added to eliminate any oxidizing effect on the potassium iodide which is used at 0.01 molar strength as the titrant. The end-point was determined with the assistance of a centrifuge which encouraged coagulation and settling. The method produced an accuracy of 0.5% or better in the presence of 5% of nickel, iridium, platinum, rhodium, tungsten, molybdenum, copper and tin. For alloys containing gold or silver a modified technique was used. In the case of samples containing gold the mixture was allowed to stand for 1 h following addition of ferrous sulphate. With silver, the chloride was precipitated and aliquots of the supernatant liquid were removed from the measured volume. The error due to the volume of silver chloride presumably fell within the 0.5% expected from the method. In a second paper[5] the iodide method was extended to apply to a series of binary alloys of palladium with platinum, rhodium, iridium, silver, gold, copper, tin, molybdenum, tungsten and nickel. A slight modification was required to remove the increased amount of nitric acid used to dissolve the alloys. For the analysis of palladium–silver alloys the hydrochloric acid concentration was adjusted to dissolve the silver chloride, in which case the titer included both silver and palladium values, with the former determined separately by iodide titration in an ammoniacal solution. This modification will have very limited application. The authors[6] also recorded a general discussion of their procedures. Improvements in the technique of detecting end-points were described; the application of a potentiometric end-point was eliminated by the presence of ferrous sulphate. Reduction to palladium by ferrous sulphate occurred at elevated temperatures, low acidity, or large excess of the ferrous ion. Under the prescribed conditions this cloud method was shown to have an end-point corresponding to the stoichiometric value and to be free of any interference from adsorption or solubility effects.

As might be expected, other well known precipitating reactions have been adapted to volumetric determinations. Those thus applied are: sodium thiosulphate, dimethylglyoxime, 1-nitroso-2-naphthol, β-furfural dioxime, cupferron and diethyldithiocarbamate. The general difficulty of course is associated with ascertaining the stoichiometric end-point. Sodium thiosulphate was used by RYABCHIKOV[7] to titrate palladium potentiometrically in a neutral solution at 80°. The end-point corresponded to complete precipitation of palladium sulphide. Dimethylglyoxime was used by KARABASH[8] for samples of 1–50 mg of palladium in less than 0.2N hydrochloric or sulphuric acids and containing no gold or divalent platinum. A small amount of quadrivalent platinum was permissible. The ethanol solution of the titrant was standardized against pure palladium. Carbon tetrachloride or chloroform was added to the palladium solution and the extracted precipitate was periodically removed during the titration. As one approached the end-point care was taken to ensure the presence of a fresh carbon tetrachloride layer whose freedom from colour was taken as indicating the stoichiometric end-point.

A more ingenious application of dimethylglyoxime was proposed by BOBTELSKY and associates[9] who have applied "heterometric" determinations to a wide variety of volumetric analyses. The method involves a continuous measurement of optical densities of the precipitating medium during the course of the titration. These data are plotted against the volume of the titrating liquid with the stoichiometric end-point taken as the straight line intersection of the horizontal curve of maximum density and the titrating curve. Undoubtedly there is much of value in this approach to volumetric methods but it should be recognized, particularly for unfamiliar titrations, that the degree to which the titrating curve requires extrapolation to the intersection of the maximum density curve there is the possibility of a corresponding error. In experienced hands this source of error can often become insignificant. There is also the limitation that the method would hardly be applicable to other than very dilute solutions. From this point of view extractive methods, or the "cloud method" used by ATKINSON can offer desirable advantages. Furthermore, within this area of small concentrations there are competitive colorimetric or spectrophotometric procedures. For the direct microheterometric determination of palladium, BOBTELSKY used palladium contents of the order of a few milligrams or less and 0.01 M dimethylglyoxime. The authors included a discussion of the effects of various buffers, complexing reagents, acidity and foreign dissolved constituents. Precipitation was complete at pH's less than 5 but at pH 11 there was complete dissolution. The examination of the effects of associated materials involved many cations which are not usually associated with the platinum metals and, inexplicably, included none of the associated platinum metals. However, with the exception of platinum and gold one would not expect a significant influence on the accuracy of the method. By a similar procedure BOBTELSKY and associates applied 1-nitroso-2-naphthol[10] and diethyldithiocarbamate[11] as titrants. Ethanol solutions of the former were used for quantities of palladium of the order of 0.2 mg or less. In the presence of uncoloured cations a red filter must be used, whereas with most coloured impurities a filter is not recommended. While chlorides should be absent, a large number of foreign cations as nitrates were without significant effect. The method is considered to be about three times more sensitive than the dimethylglyoxime procedure, although with the latter method copper did not interfere. It should be noted that the value of these heterometric investigations is not necessarily limited to the area of analytical chemistry. Interesting data concerning the compositions of precipitates corresponding to maximum density have been forthcoming. With α-nitroso-β-naphthol the rather surprising ratio of 1 palladium to 3 precipitant was recorded. With diethyldithiocarbamate[11] both palladium and gold could be determined from a single solution whose pH was close to that of pure acetic acid and which contained large excesses of ammonium chloride. Two points of maximum density were obtained, the first corresponding to the gold complex and the second to the sum of the gold and palladium complexes. If platinum is also present the second maximum density value corresponds to the sum of the three metal complexes. Determinations could be be made also in weakly basic solution by a modified and less desirable procedure. The methods are applicable to amounts of metals of the order of a milligram. Diethyldithiocarbamate had previously been used as a titrant by POLLARD[12] for weights of palladium between 0.01 to 1.0 mg. Approximately 50% hydrochloric acid must be present and sulphates, iodides and metallic impurities absent. The method involved prolonged heating in the presence of tin and tin(II) chloride, a filtration, and addition of benzene as an extractant. The carbamate titrant was added to an almost colorless solution and then the titration was continued in the presence of mercuric chloride which intensified the brown colour.

Back titrations

A variety of back titrations have been proposed for volumetric determinations of palladium. Perhaps the most generally suitable is the method recorded by MACNEVIN AND KREIGE[13]. These authors added a slight excess of EDTA to the palladium chloride solution adjusted to pH 10 ± 1, and back titrated with a standard zinc nitrate solution to the pink end-point of Eriochrome Black T. Of importance is the finding that platinum does not interfere. The fact that the method is not applicable in the presence of rhodium and osmium and that iridium and ruthenium may interfere at higher concentrations is not a particularly serious criticism of the method. These more insoluble platinum metals are often present in small proportions. The applicable range of concentration of palladium is a useful one.

An earlier EDTA titration was recorded by FLASCHKA[14]. In this method an excess of concentrated dipotassium tetracyano nickelate was added to the palladium solution which resulted in an exchange of metal to set free a stoichiometric amount of nickel ion. The latter was titrated in ammoniacal medium with EDTA to the violet of murexide indicator. The range of application was 0.3 to 3.0 mg of palladium. This method can also be a useful one.

KINNUNEN AND MERIKANTO[15] stated that the EDTA back titration, with murexide as the indicator, produced only approximate results. Alternative procedures were suggested. One method, applicable to the determination of palladium in platinum salts, involved the addition of the potassium nickel cyanide to a hydrochloric acid solution, followed by an ammonium chloride buffer, a measured excess of EDTA, ascorbic acid, and Eriochrome Black T. The excess of EDTA was titrated with manganous sulphate solution to the red colour, and then with standard EDTA to the blue colour. A second procedure, although less accurate, involved a simpler technique. With this method the excess EDTA was titrated in an acid medium with bismuth nitrate solution in the presence of pyrocatechol violet. In the author's opinion both methods are laborious and the data provided by the authors indicate neither high accuracy nor precision.

Back titrations involving prior isolation of palladium by some of the usual organic precipitants have been proposed. SYROKOMSKIĬ AND GUBEL'BANK[16] precipitated palladium by dimethylglyoxime, cupferron or furfural dioxime, then dissolved the purified complex with sulphuric acid, added a standard solution of the organic precipitant, and an excess of $V_2O_4(SO_3)_3$. The excess of the latter was titrated with standard ammonium ferrous sulphate. The method is cumbersome and is not recommended. A second procedure recorded by the authors[16] involved the isolation of palladium by precipitation as potassium or ammonium chloropalladate. Excess of ammonium ferrous sulphate was added, followed by a back titration with an oxidizing reagent. Neither the method nor the claim of non interference from small proportions of platinum is acceptable. A back titration method was proposed by GAHIDE[17]. This author worked with 12N sulphuric acid solutions containing 5 to 40 mg of palladium and precipitated the latter by a measured excess of standard salicylaldoxime. Subsequent to filtration the excess of reagent in the filtrate was hydrolyzed to form the hydroxylamine. Ferric sulphate was added and the resulting ferrous salt was titrated with standard potassium permanganate. The results recorded indicated indifferent accuracy and precision. Presumably there was little or no interference from gold or platinum. Attempts to use dimethylglyoxime and various other oximes failed.

An unusual type of back titration was proposed by BURRIEL AND PÉREZ[18] who treated a neutral palladium solution with an excess of standard potassium cyanide, then decomposed the free potassium cyanide by mercury(II) oxide and titrated the resulting hydroxide rapidly with sulphuric acid solution to a phenolphthalein end-point.

PLATINUM

The volumetric determination of platinum remains a fertile field for the analytical researcher. Very few methods have been recorded and none is recommended for other than the most restricted application. This dearth of methods finds a partial explanation in the few really satisfactory precipitating reagents, the most efficient of which have only recently been recorded. In the author's opinion, there are now available, sufficient data to encourage those investigators who entertain an interest in the development of useful volumetric methods for platinum.

About the earliest volumetric methods for platinum were recorded by HINTZ[19]; DE KONINCK[20]; and by RUPP[21]. In general, the first methods required the isolation of platinum as the potassium or ammonium salt, reduction to metal, and subsequent titration of the released chloride by silver nitrate[19,20]. RUPP[21] used a measured excess of thallous nitrate to precipitate the platinum salt which was then filtered and the excess thallous salt determined by a sodium thiosulphate titration subsequent to the addition of dichromate and potassium iodide.

As might be expected one of the earliest known reactions of platinum suggesting the possibility of a volumetric application is that with potassium iodide. This approach has occupied the attention of a number of researchers but nothing of analytical application has been forthcoming. PETERSON[22] over a half century ago claimed success with a sodium thiosulphate titration of the iodine set free by treating a platinum salt with excess potassium iodide. It was assumed that the iodide reacted with the platinum salt to produce stoichiometric quantities of platinum(II) iodide and iodine. Although the author claimed that the results were accurate this claim may be disregarded. Grinberg and co-workers[23] who have recorded a variety of volumetric methods for the platinum metals investigated the efficiency of the iodide method applied by a number of techniques. While the use of alcoholic solutions of iodine was inadmissible under all conditions, aqueous potassium iodide solution of iodine could be used to produce reasonably satisfactory results, *e.g.* 94–98% of the theoretical value. It was assumed that the reaction involved a complete exchange of iodine for chlorine in dipotassium tetrachloro platinate to produce the hexaiodo platinate. The method is slow, inaccurate, and is not recommended. Grinberg and associates recorded also a series of procedures in which permanganate was used for the direct titration of platinum and of platinum together with iridium and iron[24–31]. The mechanism of the oxidation reaction was discussed and the product of the reaction with bivalent platinum was stated as an addition of two hydroxyl groups to form $K_2PtCl_4(OH)_2$[29]. In dilute sulphuric acid solutions bivalent platinum and trivalent iridium were oxidized by permanganate to $K_2PtCl_4(OH)_2$ and K_2IrCl_6. By potentiometric titration at 80–90°, it was possible to determine platinum in the presence of iridium. By a modified procedure the end-point could also be determined visually[31]. Quadrivalent platinum could also be determined by reducing with copper(I) chloride, oxidizing the excess of the latter in air and titration with permanganate to form $(PtCl_6)^{-2}$[25]. In a second paper[28] the author and associates recorded an application of this method for the determination of total platinum and iridium. The results indicated an accuracy of about 1%. For solutions of bivalent iron, trivalent iridium and bivalent platinum two volumetric methods were discussed[24,26]. The potentiometric titration resulted in a distribution of the platinum between the iron transition and the iridium transition[26]. With the second method the iron was determined potentiometrically by a cerous sulphate titration and the sum of the three constituents was similarly determined by a permanganate titration. Methods such as these are of theoretical interest but of little practical value. Grinberg[27] also proposed a potentiometric titration for quadrivalent platinum and iridium which involved a reduction by copper(I) chloride. Separately, platinum was determined at 70° in solutions acidified to 0.05*N* HCl; iridium at 50° and 0.1*N* HCl. In determining the sum of the two quadrivalent metals, the nature of the titration curve depended upon the temperature, acidity, and the relative quantities of the metals. By control of these factors the curve showed either one or two breaks, one subsequent to reduction of iridium and the second, after the reduction of platinum. A number of investigators had devised volumetric methods based on this principle of reduction to the bivalent state. Stelling[32] reduced platinum by hydrazine and subsequently titrated potentiometrically with permanganate or bromate. Muller and Tanzler[33] used copper(I) chloride which had been standardized against potassium dichromate to titrate platinum made quadrivalent by chlorine. Ryabchikov and Nersesova[34] titrated quadrivalent platinum and iridium potentiometrically with copper(I) chloride in an atmosphere of carbon dioxide. In a later procedure the platinum was reduced by excess copper(I) chloride and subsequently oxidized with standard ceric sulphate[7]. Similarly Syrokomskiĭ and Proshenkova[35] reduced platinum by ferrous sulphate and titrated the excess with ammonium metavanadate in the presence of phenylanthranilic acid as indicator. Ferric ion was complexed by either phosphate or fluoride. Again an atmosphere of carbon dioxide was required throughout the titration. Ascorbic acid has also been used for the quantitative reduction of quadrivalent platinum[36]. With $0.2N$ hydrochloric acid solutions of platinum the excess of ascorbic acid was titrated potentiometrically with ferric chloride[36]. Diethyldithiocarbamate was used as a titrant by POLLARD[37] for the determination of 1 to 0.01 mg of platinum in the presence of gold. Applied to silver assay beads, the latter were parted in a minimum of nitric acid. Strong hydrochloric was added to prevent the precipitation of silver chloride and to dissolve platinum and gold. The addition of tin(II) chloride resulted in the precipitation of gold and the formation of the coloured platinum constituent. The mixture was shaken with benzene and titrated with diethyldithiocarbamate to form a platinum complex which passed into the benzene layer along with the precipitated gold. The end-point was indicated by a colourless aqueous-acid layer. An adaptation allowed the determination of both gold and platinum.

In order to avoid interference from palladium, POLLARD[38] substituted tin(II) bromide for the chloride to precipitate both palladium and gold. This method was also applied to silver-assay beads. Subsequent to parting by nitric acid the silver, platinum and gold were dissolved in a strong hydrobromic acid solution. The resulting nitrosyl bromide and bromine were destroyed by hydroxylamine hydrochloride. Any of the insoluble platinum metals were removed at this stage; tin(II) bromide was added to produce the yellowish-brown platinum complex and to isolate metallic gold and palladium. The addition of benzene and subsequent titration with the carbamate to a colourless end-point permitted the direct determination of platinum. The data provided indicated very satisfactory accuracy and in the opinion of the present author the method is a useful one. There is here one of the few instances when the investigator has not ignored the difficulties incident to the methods of dissolution and separation encountered in analytical practice.

RHODIUM

Only two acceptably complete volumetric procedures for rhodium have been recorded. SYROKOMSKIĬ AND PROSHENKOVA[39] used a sodium bismuthate oxidation of rhodium in a previously fumed sulphuric acid solution. Subsequent to a filtration the quinquevalent rhodium was titrated with Mohr's salt to the yellow-green end-point of phenylanthranilic acid. The authors reported no interference from other platinum metals. However, MCBRYDE AND CLUETT[40] found that in the presence of iridium the reduction of sodium bismuthate was accelerated and rhodium values were low. The oxidation of iridium proceeded to an indefinite stage. These data suggest a very restricted area of application and furthermore, one can expect difficulty with the slowly developing end-point. The precipitating reagent thionalide was applied volumetrically by KIENITZ AND ROMBOCK[41]. The rhodium solution was fumed to remove chloride ion which interfered by producing a precipitate of the rhodium thionalide mixed with rhodium chloride. The method involved the precipitation of rhodium by excess of thionalide, and titration of the latter by standard iodine to a slight excess of the latter, and back titration with sodium thiosulphate. The method requires a simple technique but is less accurate than existing gravimetric methods. Ascorbic acid has also been used as a titrant for quadrivalent rhodium.

PSHENITSYN AND PROKOF'EVA[42] applied this reagent to the volumetric determination of both rhodium and iridium.

IRIDIUM

Approximately one dozen volumetric methods for iridium have been recorded. Most of these are potentiometric titrations which involve the oxidation of iridium from the trivalent state or the reduction of iridium from the quadrivalent state. In a few cases visual observation of the end-point was considered feasible. None of these latter procedures is recommended.

SHOW-CHOW AND YOST[43] claimed good results from a sodium thiosulphate titration of the iodine liberated from a hydrochloric acid solution containing quadrivalent iridium and excess of potassium iodide. This procedure was unacceptable to GRINBERG and co-workers[28,31] and this decision would seem to be the more acceptable. GRINBERG used copper(I) chloride to produce trivalent iridium. The solution was air oxidized to eliminate the cuprous copper and titrated potentiometrically with potassium permanganate[28]. The results were accurate to about 1%. RYABCHIKOV AND NERSESOVA[34] titrated quadrivalent iridium potentiometrically with copper(I) chloride in an atmosphere of carbon dioxide. The method is relatively unsatisfactory due to the sensitivity to oxidation of the titrant. Various authors have used hydroquinone or related compounds as reducing reagents[7,44-47]. RYABCHIKOV[7,47] standardized hydroquinone against an iridium solution of known value. Chlorine was used to ensure the initial quadrivalent state. MILAZZO AND PAOLONI[45] used hydroquinone as a titrant with *o*-dianisidine as an indicator. PSHENITSYN AND PROKOF'EVA[46] used diphenylamine as an indicator. Hydroquinone was used by POLLARD[48] for the determination of quantities of iridium of the order of 0.1 to 0.001 mg. Subsequent to the isolation of iridium by methods, some of which are not consistently reliable, the solution of iridium was treated with a lithium sulphate–sulphuric acid reagent, perchloric acid, and dichlorobenzidine indicator, and heated according to an accurately measured time schedule to produce the usual mauve iridium constituent. This solution was titrated with hydroquinone, previously standardized against pure iridium, to the disappearance of the yellow colour of the dichlorobenzidine indicator, a drop of which was added near the completion of the titration. A confirming determination should always be made by re-oxidation and a second titration. The authors' data indicate a surprising degree of accuracy and precision. The mauve colour development recommended is comparable to that which found later application in spectrophotometric methods and the experience with this method gained by the author and co-workers does not encourage a recommendation for this volumetric method. The susceptibility of colour intensity to the various factors which influence the equilibria involved in the production of this mauve colour suggest the need for further data. Until these data are provided the method will remain suspect.

Titanium(III) chloride[40,46] and tetrapotassium hexacyanoferrate[45,49] have also been applied as titrants. Ferrous sulphate and Mohr's salt have also been used frequently for the volumetric determination of iridium. GRINBERG AND PTITZUIN[31] were able to follow potentiometrically the reduction of sulphuric acid solutions of quadrivalent iridium by Mohr's salt, and also quantitatively to re-oxidize the trivalent iridium with potassium permanganate.

Both of these methods were recommended by KOZYAR[50] to produce an accuracy of 0.2%. There was no interference from quadrivalent platinum, trivalent rhodium and divalent palladium. McBRYDE AND CLUETT[40] used the ferrous sulphate reduction of solutions of iridium previously fumed with sulphuric acid and then oxidized with ceric sulphate for a period of about 10 h. A direct oxidation of iridium(III) was unsuccessful due probably to the slowness of the reaction. Titanium(III) chloride could also be used for the reduction titration. Platinum and rhodium did not interfere. Ruthenium and osmium could be removed by prior oxidation; with the latter metal, nitric acid was added to produce the volatile octovalent oxide. In addition to the end-point indicated by the reduction of cerium(IV) sulphate there were two end-points involved in the complete reduction of iridium to the trivalent state. The first represented a one equivalent reduction and the second step a 1/2 equivalent reduction. Of advantage is the fact that just prior to the final end-point the solution becomes colourless. The method was applicable to quantities between 2 and 20 mg and the accuracy for the larger samples was of the order of 1%.

PSHENITSYN and co-workers[42,46] also used ferrous sulphate as a titrant with *o*-phenanthroline as an indicator. In a later publication[42] ascorbic acid was used although the errors were as high as 5%. Platinum and rhodium did not interfere.

Of the volumetric methods available for iridium the author recommends the reduction by ferrous sulphate. With all of the methods a degree of isolation is required. While no reference to the influence of gold is included for the methods it is probable that all of the recorded reducing reagents will precipitate this metal. Prior treatment of the solution by fuming with sulphuric acid would probably remove both gold and platinum as metals with the possibility of some slight dissolution of the latter metal. Of interest in this volumetric method is the fact that rhodium is not generally an interfering element and the advantage of this factor lies in the frequent association of rhodium and iridium in somewhat comparable proportions.

RUTHENIUM

Very few methods for the determination of ruthenium have been recorded. Until recently no reliable method for the quantitative recovery of the metal was known. Simultaneously with improvement in the precipitation as a hydrated oxide there appeared a volumetric method which involved a titration with tin(II) chloride. The procedure entailed a reduction of ruthenium to the trivalent state by an excess of standard tin(II) chloride which was back titrated with iodine in the presence of starch. HOWE[51] used this method but reported a tendency toward low values for which no satisfactory explanation was available. CROWELL AND YOST[52] used two volumetric methods during their investigation of the various oxidation states of dissolved ruthenium halides. In one procedure an excess of potassium iodide was added to ruthenium chloride in hydrochloric acid solution and the liberated iodine was titrated with sodium thiosulphate. The second method required a potentiometric titration of quadrivalent ruthenium with titanium(III) chloride. Their data indicate a quantitative reduction from the quadrivalent to the trivalent state with solutions previously oxidized with chlorine. In the absence of the latter the discontinuity in the titration curve suggested the existence of both the trivalent and quadrivalent states. Since this publication was not directed toward the analytical field, few of the necessary techniques were discussed. The titanium(III) chloride titration was also examined by PSHENITSYN AND GINZBURG[53], who stated that two potential jumps were present in their titration curve. The first, corresponding to a change of one half an equivalent weight of ruthenium, and resulting from an intermediate equilibrium mixture of constant proportions of quadrivalent and trivalent ruthenium, made possible by a high rate of equilibrium. The second break corresponded to the formation of trivalent ruthenium. Comparable results were obtained from both discontinuities.

OSMIUM

One of the first volumetric methods for the determination of osmium was developed by KLOBBIE[54] who added potassium iodide to a sulphuric acid solution of the octavalent oxide and titrated the liberated iodine with sodium thiosulphate. The author claimed an accuracy of 0.01%. This claim is unacceptable. The end-point in the green solution cannot be determined with good precision. For small amounts of osmium the usual modification of reducing the strength of the sodium thiosulphate is ineffective because of the considerable decrease in the time of reaction. With large amounts of osmium the detection of the end-point becomes increasingly difficult because of the deeper colour of the reduced osmium. CROWELL AND KIRSCHMAN[55] modified the method to avoid air oxidation of the potassium iodide. SAITO[56] proposed the use of benzene as an aid in ascertaining the end-point. RYABCHIKOV[47,57] used the iodide method in a potentiometric titration. This author[7] also titrated directly, by a potentiometric method, an alkaline solution of octovalent osmium to produce a sexivalent state. The drop in potential at the equivalence point, while not large, was quite distinct. CROWELL *et al.*[55,58,59] applied this approach to develop a number of volumetric methods for osmium. Hydrazine sulphate[55] was used a titrant resulting in a reduction of octovalent osmium to the quadrivalent state in a hydrobromic acid solution whose final acidity was 1.5*N*. To avoid the error due to the volatility of osmium in an acid medium the authors prepared sealed glass tubes containing the osmium added as an alkaline solution, together with hydrobromic acid, and a slight deficiency of hydrazine sulphate determined by a prior titration. The reaction was induced by a boiling period after which the tube was broken, washed out with hydrobromic acid solution and titrated potentiometrically at 70°. The method was applied satisfactorily to amounts of osmium of the order of 2 mg. Compared to a gravimetric and the volumetric iodide method the results from three methods agreed within 0.3%. In later publications CROWELL[58-60] reported a volumetric method for octovalent and for quadrivalent osmium based on the difference in equilibria of osmium salts in dilute and concentrated solutions of hydrobromic acid. In 8*N* hydrobromic acid the reaction was practically complete in the direction of formation of quadrivalent osmium and bromine. Potentiometric titration with hydrazine sulphate of the bromine produced permitted the determination of octovalent osmium with an accuracy of about 0.2%. The octovalent oxide in an alkaline medium was sealed into a pyrex tube containing an ice-cold solution of concentrated hydrobromic acid; the tube was heated, cooled and broken into a slight deficiency of hydrazine sulphate solution and the titration of the residual bromine was then completed potentiometrically. With solutions of osmium containing about 0.1*N* hydrobromic acid, quadrivalent osmium reacted in the direction opposite to that in 8*N* acid. The osmium could then be determined by a similar measurement of the bromine consumed. In this procedure the sealed tube contained a measured volume of standard bromine solution. Titanium(III) chloride was also used as a titrant[60] to produce quadrivalent and trivalent osmium, but its relative instability makes it a lesser desirable standard than hydrazine sulphate. Furthermore this method is quite inaccurate. All of these techniques are cumbersome and since the accuracy depends upon forcing equilibria to practical completion, one cannot use these methods with confidence. They will find little application in general practice. In the author's opinion this is also true of the chromous sulphate method recorded by Crowell and Baumbach[59]. The titrant is exceedingly sensitive to oxidation and the technique involved in the procedure, while capable of yielding acceptable results in the hands of an experienced operator, will not encourage any extensive application.

A back titration method was recorded by Syrokomskiĭ[61]. The octovalent osmium dissolved in $4-6N$ sulphuric acid was reduced to the quadrivalent state by passing the solution over bismuth granules. Quantitative oxidation to the sexivalent state was accomplished by the addition of a measured excess of ammonium *meta*vanadate. This excess was determined by a ferrous sulphate titration with phenylanthranilic acid. Any lack of accuracy by this procedure finds some compensation in relative simplicity of operation.

SUMMARY

The published methods for the volumetric determination of the six platinum metals have been appraised. The lack of generally applicable and accurate methods is emphasized. No volumetric method has been recorded for the direct application to solutions of platinum metals, ores, concentrates or natural alloys, and only a few for determinations in synthetic alloys such as fire assay beads. Volumetric methods for the platinum metals are characterized by the absence of data concerning methods of dissolution.

RÉSUMÉ

L'auteur passe en revue les méthodes volumétriques publiées pour le dosage des six métaux de la mine de platine. On constate un manque de méthodes générales et précises, ainsi que de données concernant les mises en solution.

ZUSAMMENFASSUNG

Die bekannten volumetrischen Methoden zur Bestimmung der 6 Metalle der Platingruppe werden einer kritischen Betrachtung unterzogen. Es wird das Fehlen von genauen, allgemein anwendbaren Methoden sowie Vorschriften zur Auflösung dieser Metalle hervorgehoben.

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THE DETERMINATION OF TITANIUM WITH EDTA

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The work of SCHWARZENBACH and co-workers has led to many applications of EDTA* in analytical chemistry. A large number of publications have appeared in the literature presenting useful data and methods for the application of EDTA to analytical problems.

This work was initiated to clarify some conflicting opinions on the conditions under which EDTA could be used for the determination of titanium. A method has been proposed[1] for the determination of titanium in which an excess of EDTA is added to a titanium solution and the excess determined by a back titration with standard copper. Pyrocatechol violet is used as an indicator, and the solution is buffered at a pH of 5.3-6.0 with pyridine acetate. It was reported that the indicator color change was irreversible.

The author has tried this procedure as well as buffering at pH of 4-5 with sodium acetate-acetic acid[2] with little success. The failure of the method can be attributed to the formation of a hydrous oxide precipitate which results in a release of EDTA from the titanium-EDTA complex. This was quite evident from the appearance of a precipitate or cloudiness in the solution and from the values obtained on a standard titanium solution. The results shown in Table I demonstrate the unsatisfactory values obtained by back titration with copper over the pH range of 4-6.

The condition mentioned above is even more serious in the actual analysis of a metallurgical sample. In this laboratory the methods of separation of titanium from interfering elements usually finish with the titanium present in strong hydrochloric or hydrofluoric acid. In either case the acid must be removed. This is usually done by the

TABLE I

TITRATION OF Ti WITHOUT PEROXIDE

Sample No.	*Cu used*	*Cu required*	*Error mg Ti*
1	3·99	2·94	1·5
2	3·99	2·94	1·5
3	3·77	2·94	1·2
4	4·30	2·94	2·0
5	3·73	2·94	1·1
6	3·74	2·94	1·1
7	3·77	2·94	1·2

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* Ethylenediaminetetraacetic acid.

addition of a few ml of sulfuric acid followed by evaporation to copious fumes. Attempts to use the previously mentioned procedure invariably resulted in more severe precipitation of titanium because of the necessity of neutralizing the excess acid.

PECSOK AND MAVERICK[3] have studied the titanium-EDTA complex polarographically. They suggest that at a pH greater than 2, the complex contains oxygen. The half-wave potential is pH-dependent over the pH range of 2-8, and the solutions were often visually cloudy.

It is apparent that the interference in the method is caused by a side reaction, namely, the precipitation of hydrous titanium oxide. A possible mechanism for this side reaction is the initial formation of a titanium-EDTA-oxygen (or hydroxy) complex followed by polymerization through oxygen bridges. This process would continue by the formation of sufficiently large aggregates to form colloidal hydrous titanium oxide and finally result in a precipitate. This would release EDTA in solution and produce an error in the back-titration.

If this mechanism is correct, the reaction could be inhibited by substituting some other group in the complex in place of oxygen or hydroxy ions.

In order to conform to the stipulation that the titanium would be present in a concentrated sulfuric acid after its separation, a substituent group was desired which would allow neutralization of the titanium solution from concentrated sulfuric acid to a pH of approximately 4.8 without interfering with the 1:1 relationship between EDTA and titanium. Tartaric acid and hydrogen peroxide were selected for a preliminary investigation. Tartaric acid masked titanium almost completely, which made its use in the titration impossible. Hydrogen peroxide proved promising and was investigated further. It has been reported that hydrogen peroxide does not interfere in the titration[1,2], but in both papers the recommended procedures do not include hydrogen peroxide in the method. SWEETSER AND BRICKER[4] determined titanium with EDTA by means of a back titration with an iron solution, using a spectrophotometric end-point. The titration was performed at a pH of 1.7 but the results were 0.7-1.5 % low. They suggest that the error is caused by the displacement of titanium from its EDTA complex by iron[4]. They also found that the titanium is not displaced by the iron when peroxide is present at a pH of 1.7 and that a 1:1 titanium-EDTA complex is formed.

EXPERIMENTAL

To aliquots of the standard titanium in a 250-ml beaker were added 3 drops of 30 vol. % hydrogen peroxide, an excess of EDTA, and 10 ml of sodium acetate-acetic acid buffer. The resulting orange solution was diluted to approximately 100 ml and, while stirring with a magnetic stirrer, the solution was neutralized to a pH of 4-5 by the addition of a 50 % sodium hydroxide solution from a polyethylene wash bottle. After neutralization, eight drops of PAN [1-(2-pyridylazo)-2-naphthol; 0.05% in ethanol] were added and the solution back-titrated with a standard copper solution. The color change at the end-point was from orange to orange-red. The results of analysis of the standard solution are shown in Table II. The method was applied to alloy samples (after separation of titanium) by the method below.

PROCEDURE

To the hydrofluoric or hydrochloric acid titanium fraction in an appropriate vessel add 10 ml of 1 : 1 sulfuric acid and evaporate to copious fumes. Cool to room temperature, add 10-15 g of ice (from distilled water) followed immediately by 3 drops of 30 volumes hydrogen peroxide. (At this point, for large amounts of titanium, transfer the solution to a volumetric flask, dilute to volume with water and take an appropriate aliquot.) Add a 5–10 ml excess of EDTA solution, dilute to approximately 100 ml with water, neutralize with 50% sodium hydroxide (to pH of 4–5) and add 8 drops of PAN indicator. Back-titrate with standard copper solution to color change from orange to orange-red.

TABLE II

TITRATION OF Ti WITH PEROXIDE

Sample No.	*mg Ti present*	*mg Ti found*	*Error mg Ti*
1	10.28	10.26	0.02
2	10.28	10.25	0.03
3	10.28	10.25	0.03
4	10.28	10.26	0.02
5	10.28	10.27	0.01
6	10.28	10.23	0.05
7	10.28	10.20	0.08
8	10.28	10.20	0.08
9	10.28	10.20	0.08

DISCUSSION

The addition of peroxide to the titanium solution containing EDTA before adjusting the pH definitely inhibits the precipitation of hydrous titanium oxide. This is evident by the fact that the solution remains clear throughout the titration. One would normally expect a hydrogen complex, such as TiHY, in strong acid solution; however, in view of the orange color present in strong acid (with hydrogen peroxide present) it appears that the titanium complex contains one or more peroxide molecules in place of the hydrogen ion. The orange color present in the titanium–EDTA–peroxide system at a pH of 4–5 indicates that one or more peroxide molecules also are present in the complex under these conditions. Furthermore, since precipitation occurs in the absence of hydrogen peroxide but does not occur in its presence, it is suggested that the hydroxy (or oxygen) ion is displaced by peroxide, which inhibits the mechanism of precipitation.

The indicator color is reversible when peroxide is used. In experiments without peroxide, in which precipitation invariably took place, the color change with pyrocatechol violet was irreversible. This phenomenon can be explained by the formation of colored lakes by the indicator and hydrous titanium oxide or by the irreversible adsorption of the copper indicator complex on the surface of hydrous titanium oxide.

It is well known that with PAN and pyrocatechol violet the color change during a back titration with copper is reversible. In determinations in which an irreversible color change occurs during a back-titration with copper, it should be taken as evidence that some side reaction is taking place and the method should be investigated more thoroughly before applying it to analytical problems in the laboratory.

SUMMARY

The determination of titanium EDTA by means of a back-titration with standard copper has been investigated. The phenomenon of an irreversible color change has been eliminated by the addition of hydrogen peroxide prior to the addition of EDTA and adjustment of pH.

It is theorized that peroxide displaces the hydroxyl (or oxygen) ion in the hydroxy–EDTA–titanium complex and thus inhibits precipitation.

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RÉSUMÉ

L'auteur étudie le dosage du titane par l'acide éthylènediaminotétracétique par titrage indirect au moyen d'une solution étalon de cuivre. Une addition de peroxyde d'hydrogène permet d'éviter le phénomène du changement de coloration irréversible. Le peroxyde déplace l'ion hydroxyle (ou l'oxygène) du complexe hydroxy-EDTA-titane et empêche ainsi la précipitation.

ZUSAMMENFASSUNG

Es wird die Bestimmung von Titan mit EDTA durch indirekte Titrierung mit einer Standard-Kupfersalzlösung beschrieben. Ein Zusatz von Wasserstoffsuperoxyd verhindert das Auftreten eines irreversiblen Farbumschlages. Vermutlich wird das OH-(oder Sauerstoff) Ion des Hydroxy-EDTA-Ti Komplexes durch das Peroxyd verdrängt, wodurch die Bildung eines Niederschlages verhindert wird.

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THE DETERMINATION OF LITHIUM IN LITHIUM-MAGNESIUM ALLOYS

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As would be expected from the similarity in the size to charge ratio of lithium and magnesium, the separation of these two elements by gravimetric methods is difficult. The methods generally used for the determination of lithium are based on precipitation as an insoluble aluminate, fluoride, or phosphate. Magnesium interferes with these procedures.

Lithium is conveniently determined in many materials by flame photometry; however, it has been reported that the characteristic emission of lithium is quenched by magnesium[1]. In view of the unfavorable ratio of magnesium to lithium in the alloys under consideration, the application of the flame photometer was not investigated.

Recent advances in the applications of ion exchange resins in analytical chemistry have shown excellent results in the separation of elements with closely related properties. The separation of rare earth elements best illustrates this fact.

Samuelson and Schramm[2] have suggested a method for the separation of sodium and potassium from the transition elements by using an anion exchange resin in the citrate form to absorb the heavy metals. The alkali metals in the form of their citrates are passed through a second column, coupled to the first, to convert the alkali metal

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salts to hydroxides. The hydroxides were determined by titration with a standard acid. Magnesium accompanies the alkali metals[3].

In a subsequent publication[4], EDTA was substituted for citrate in order to separate calcium and magnesium from the alkali metals. Lithium and magnesium could not be separated in aqueous solution. By lowering the pH in the resin phase and by eluting with a 60% ethyl alcohol solution, the separation of lithium and magnesium was accomplished.

The favorable relationship in the absorption of lithium and hydrogen by a strongly acidic cation exchange resin indicated that a suitable separation of lithium and magnesium could be attained on a cation exchange resin. The separation on a cation exchange resin, by eluting the lithium with dilute acid, would simplify the regeneration of the column and provide a rapid separation.

EXPERIMENTAL

Initial experiments were conducted with synthetic samples. These samples consisted of aliquots from a standard lithium solution to which were added sufficient magnesium carbonate to approximate the magnesium content in the alloys of interest. Excess hydrochloric acid was added to each sample to dissolve the magnesium carbonate and the samples taken to dryness on a hot plate. The samples were redissolved in water and sufficient dilute hydrochloric acid added to give a clear solution. The sample solution was then transferred to an ion exchange column (1 cm I.D. × 50 cm long) containing a strongly acidic ion exchange resin (H^+ form, 100–150 mesh) with water. After all the sample was rinsed onto the resin with water, the lithium was eluted with 0.5*N* hydrochloric acid. The eluate was checked frequently for lithium by catching a drop on a platinum wire and applying the flame test for lithium. It was observed that the eluate from washing the sample into the resin with water never contained lithium and that the first 150-ml fraction of 0.5*N* hydrochloric acid contained all the lithium. This was determined with several different columns.

The eluate containing the lithium was evaporated to dryness, dried for 1 h in an oven at 110° and dissolved in 50 ml of water. The lithium was determined by titration of the chloride from the lithium chloride residue with silver nitrate. The results of eight synthetic samples are shown in Table I.

TABLE I

Sample No.	*Li present mg*	*Li found mg*	*Mg present mg*
1	10.14	10.12	90
2	10.14	10.11	90
3	10.14	10.23	90
4	10.14	9.97	90
5	10.14	10.19	90
6	10.14	10.05	90
7	10.14	10.18	90
8	10.14	9.95	90
	average	10.10	

PROCEDURE

Dissolve a 0.5-g sample in dilute hydrochloric acid and evaporate to dryness. Dissolve the residue in water and sufficient hydrochloric acid to give a clear solution. Transfer to a 100-ml volumetric flask and dilute to volume with water. Transfer a 10-ml aliquot to the ion exchange column and wash the sample into the resin with water. Discard the eluate from the washings and elute the lithium with 150 ml of 0.5*N* hydrochloric acid into a 250-ml beaker. Evaporate the so-

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lution containing the lithium to dryness and dry the beaker in an oven at 110° for 1 h. After cooling, dissolve the residue in water and titrate the chloride with silver nitrate.

$$\% \text{ Li} = \frac{(\text{vol. of AgNO}_3)\ (N \text{ of AgNO}_3)\ (\text{mol. wt. of Li}) \times 100}{(\text{sample wt.})\ (1/10)}$$

The column is prepared for the next sample by eluting the magnesium with 4*N* hydrochloric acid (2 column volumes) followed by washing with water until neutral.

DISCUSSION

The volume used for the elution of lithium was suitable for the columns and the resin used in this work. Since the particle size of resins varies somewhat from one lot to the next, it is necessary to determine the volume of eluate which contains the lithium when a different lot of resin is used as well as for columns with different dimensions. The resin was supported in the columns in this investigation by means of a coarse glass frit. The flow rate was restricted only by the normal back pressure in the column and varied from 10 to 11 ml per min for the columns used.

A precaution which must be taken into account is the calculation of per cent lithium. Some caution is needed in the analysis of lithium today since the lithium routinely available may consist of an unusual mixture of isotopes. With elements of low atomic weight, such as lithium, variations from the normal isotopic mixture may cause significant errors.

In the analysis of alloys small amounts of heavy metals will remain in the column with magnesium provided the solution is acidified slightly before diluting to volume. Failure to add sufficient acid to obtain a clear solution may result in colloidal aggregates which may pass through the column.

SUMMARY

An ion exchange method has been developed for the determination of lithium in lithium–magnesium alloys. Lithium is separated from magnesium by eluting lithium from a strongly acidic cation exchange resin with 0.5*N* hydrochloric acid. Attention is drawn to the fact that considerable quantities of unusual mixtures of lithium isotopes are in existence, and may cause significant errors if their composition is unknown to the analyst.

RÉSUMÉ

Une méthode par échange d'ions est proposée pour le dosage du lithium dans des alliages lithium–magnésium. Le lithium est séparé du magnésium par élution au moyen d'acide chlorhydrique 0.5*N*.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Lithium in Lithium–Magnesium Legierungen mit Hilfe von Ionen-Austauschern beschrieben. Die Trennung vom Magnesium erfolgt durch Eluieren mit 0.5*N* Salzsäure.

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A SYSTEMATIC STUDY OF INSOLUBLE SUBSTANCES. II

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Antimonates

In earlier publications[1-3] from this laboratory dealing with the behaviour of insoluble substances, a number of substances have been reported that become resistant towards the action of acids on heating to a high temperature. None of the antimonates has so far been reported as being insoluble in acids but our investigations have shown that the antimonates of many metals if heated to 900° for two hours in a muffle furnace become very difficultly soluble in concentrated acids.

With regard to the preparation of antimonates the general method followed consisted in adding an aqueous solution containing the chloride or sulphate of the metal to a hot dilute aqueous solution of potassium dihydropyroantimonate. An aqueous solution of potassium dihydropyroantimonate is regarded as potassium dihydroantimonate[4], KH_2SbO_4 and the precipitates obtained by precipitation may thus be regarded as dihydroantimonates which on heating to a high temperature change into metantimonates.

$$NiCl_2 + 2\ KH_2SbO_4 \rightleftharpoons Ni(H_2SbO_4)_2 + 2\ KCl$$

$$Ni(H_2SbO_4)_2 \xrightarrow{\text{Heat}} Ni(SbO_3)_2$$

The precipitated antimonates were filtered and washed with water. All the antimonates prepared by the above method were found to be soluble in acids but were rendered insoluble on heating to 900° for two hours in a muffle furnace. Of course, before they were subjected to the standard acid treatment, all of them were treated with dilute hydrochloric acid to extract any impurity that may be present.

To measure the extent of insolubility of the heated antimonates, the procedure outlined in an earlier paper[3] of this series was followed. After the acid treatment the heated antimonates should be washed with dil. HCl and not with pure water as some of them tend to form a suspension with pure water.

The heated antimonates were also analysed to determine their percentage composition. Weighed amounts of the substances were fused with caustic potash, potassium nitrate being added when chromium was present and potassium carbonate in the case of calcium, strontium or barium. Sodium salts alone or in combination with potassium salts cannot be used for fusion because of the precipitation of sodium antimonate which is much less soluble than the potassium salt in water. Antimony was estimated in the filtrate as antimony pentasulphide[5] and the other metals by well-known methods. Percentage composition of the heated antimonates was calculated and found to be the same as that of the metantimonates (without the combined water) reported in the literature. Only in the case of aluminium did the composition of the heated substance correspond to a mixture of ortho- and metantimonates, and in the case of zirconium to that of zirconyl pyroantimonate.

TABLE I

ANTIMONATES

Name of the compound	*Two hours ignition at 900°*		*Nine hours additional ignition at 900°*		*0.01 g of the substance in one standard acid treatment*	*Formula given in literature*	*Formula found*
	Percentage left undissolved in		*Percentage left undissolved in*				
	one standard acid treatment	*five standard acid treatments*	*one standard acid treatment*	*five standard acid treatments*			
1. Beryllium metantimonate	94.6	86.6	96.8	92.3	Does not dissolve completely	$Be(SbO_3)_2$	$Be(SbO_3)_2$
2. Magnesium ,,	99.3	98.4	—	—	,,	$Mg(SbO_3)_2$	$Mg(SbO_3)_2$
3. Zinc ,,	99.5	99.4	—	—	,,	$Zn(SbO_3)_2$	$Zn(SbO_3)_2$
4. Cadmium ,,	98.4	93.8	98.8	95.3	,,	$Cd(SbO_3)_2$	$Cd(SbO_3)_2$
5. Chromium ,,	97.4	93.4	98.0	94.9	,,	$Cr(SbO_3)_3$	$Cr(SbO_3)_3$
6. Manganese ,,	99.7	98.0	—	—	,,	$Mn(SbO_3)_2$	$Mn(SbO_3)_2$
7. Cobalt ,,	99.3	99.0	—	—	,,	$Co(SbO_3)_2$	$Co(SbO_3)_2$
8. Nickel ,,	99.8	99.7	—	—	,,	$Ni(SbO_3)_2$	$Ni(SbO_3)_2$
9. Copper ,,	99.8	99.0	—	—	,,	$Cu(SbO_3)_2$	$Cu(SbO_3)_2$
10. Calcium ,,	99.2	99.0	—	—	,,	$Ca(SbO_3)_2$	$Ca(SbO_3)_2$
11. Strontium ,,	99.6	99.4	—	—	,,	$Sr(SbO_3)_2$	$Sr(SbO_3)_2$
12. Barium ,,	68.4	66.0	95.8	83.1	,,	$Ba(SbO_3)_2$	$Ba(SbO_3)_2$
13. Aluminium antimonate	99.9	99.6	—	—	,,	$\begin{bmatrix}AlSbO_4\\Al(SbO_3)_3\end{bmatrix}$	$\begin{bmatrix}AlSbO_4\\Al(SbO_3)_3\end{bmatrix}$
14. Thorium metantimonate	98.6	96.2	99.5	98.0	,,	—	$Th(SbO_3)_4$
15. Zirconyl pyroantimonate	98.4	97.6	98.5	97.6	,,	$Zr_2Sb_2O_9$	$Zr_2Sb_2O_9$
16. Uranium antimonate	86.4	76.5	91.4	80.6	,,	$UO_2{\cdot}1.22Sb_2O_5$	$UO_2{\cdot}1.22Sb_2O_5$

Stannates and arsenates

The behaviour of the corresponding arsenates and stannates was also investigated but though the difficultly soluble salts are precipitated on mixing the solution of sodium stannate and disodium hydrogen arsenate with the metallic salt solution, unlike antimonates, they are not rendered insoluble in acids on heating to a high temperature. The stannates decompose leaving a residue of stannic oxide, while arsenates form pyroarsenates which are soluble in acids. The only exceptions are the arsenates of the three metals reported in the previous paper[3] and that of tin which also becomes insoluble to the extent of about 99%.

To see how far these insoluble compounds would be affected when preparing the sodium carbonate filtrate for the detection of the anions, the heated compounds were boiled with about 10% sodium carbonate solution for ten minutes. It was found that most of the heated compounds were not at all affected by this treatment. The exceptions were the arsenates of zirconium, titanium and tin, which are attacked to a slight extent and manganic metaphosphate which is completely decomposed.

SUMMARY

The antimonates of Be, Mg, Zn, Cd, Cr, Mn, Co, Ni, Cu, Ca, Sr, Ba, Al, Th, Zr and U when heated to 900° were found to become sufficiently resistant to the standard acid treatment to be considered insoluble. The corresponding stannates do not become insoluble on being subjected to this treatment. The corresponding arsenates with the exception of those of Zr, Ti, Cr and Sn also do not become insoluble on being heated.

RÉSUMÉ

Les antimoniates de Be, Mg, Zn, Cd, Cr, Mn, Co, Ni, Cu, Ca, Sr, Ba, Al, Th, Zr et U, chauffés à 900° résistent suffisamment au traitement par un acide pour être considérés comme insolubles, contrairement aux stannates et aux arsénates correspondants (à l'exception de ceux de Zr, Ti, Cr et Sn).

ZUSAMMENFASSUNG

Die Antimonate von Be, Mg, Zn, Cd, Cr, Mn, Co, Ni, Cu, Ca, Sr, Ba, Al, Th, Zr und U werden durch Erhitzen auf 900° genügend säure-unempfindlich, dass sie als „unlöslich" bezeichnet werden können. Die entsprechenden Stannate and Arsenate (letztere mit Ausnahme von Zr, Ti, Cr und Sn) bleiben nach dieser Behandlung säure-löslich.

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SEPARATIONS INVOLVING PALLADIUM

SEPARATION OF LEAD, BISMUTH, CADMIUM, THALLIUM, COPPER, COBALT AND NICKEL FROM PALLADIUM

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In the new and more comprehensive scheme of qualitative analysis[1], the use of 1% dimethylglyoxime to separate palladium from other metals of the copper group has been recommended. In the present investigation an attempt has been made to carry out this separation on a quantitative basis and quite satisfactory results have been obtained. The quantitative separation of palladium from rhodium with dimethylglyoxime is already well-known and has been omitted.

EXPERIMENTAL

Separation of palladium from lead

Measured volumes of standard solutions of palladium chloride[2] and lead acetate[3] were mixed, treated with 20 ml of 12*N* hydrochloric and diluted to 100 ml to adjust the concentration of acid to 2–3*N*. The mixture was treated with 20 ml of 1% dimethylglyoxime solution in alcohol and allowed to stand for an hour with occasional shaking to complete the precipitation of palladium. The precipitate of palladium complex was filtered through a weighed sintered glass crucible (porosity 4), washed with hot water containing a few drops of 2*N* hydrochloric acid (the filtrate being reserved for the estimation of lead), then with 50% alcohol, dried at 110° for an hour and weighed.

The filtrate was concentrated to a small volume and organic matter destroyed by evaporating to fumes with sulphuric acid and concentrated nitric acid. The solution was diluted to 25 ml and again evaporated to fumes to destroy nitroso-compounds which may interfere in the subsequent precipitation of lead as sulphide. The free acid was neutralized with ammonia (sp.gr. 0.88) and the precipitate of lead sulphate dissolved by adding ammonium acetate (solid). The solution was cooled in ice and treated with 20–30 ml of 2*N* sodium sulphide reagent[4] followed by enough 6*N* acetic acid to render the mixture acid. The mixture was heated to boiling to completely precipitate lead as sulphide. The precipitate of lead sulphide was weighed after suitable treatment.

In the filtrate from palladium, lead can also be estimated as sulphate, but the procedure of evaporating to fumes with H_2SO_4–HNO_3 has to be repeated 2–3 times in order to remove hydrochloric and acetic acids completely.

45–58 mg of palladium could be separated from 49–62 mg of lead. The metals were recovered with an accuracy of: Pd 0.0 to −0.27% and Pb 0.0 to −0.29%.

Separation of palladium from bismuth and cadmium

Standard solutions of palladium chloride and bismuth chloride[5] or cadmium sulphate[5] were used. The procedure given for the separation of palladium from lead was followed. Palladium was estimated as the dimethylglyoxime complex. In the filtrate bismuth and cadmium were estimated as sulphides. The precipitate of cadmium sulphide was washed thoroughly with alcohol and ether successively, dried at 105° for 1 h and weighed.

45–58 mg of palladium could be separated from 46–59 mg of bismuth or 44–56 mg of cadmium. The metals were recovered with an accuracy of:

Pd 0.0 to −0.26% and Bi +0.06 to −0.3%;
Pd 0.0 to −0.28% and Cd 0.0 to −0.36%.

Separation of palladium from thallium, copper, cobalt or nickel

Standard solutions of palladium chloride, thallium sulphate[6], copper sulphate, cobalt sulphate[7], and nickel sulphate[8] were used. The procedure given for the separation of palladium from lead was followed. Palladium was estimated as the dimethylglyoxime complex.

In the case of thallium, copper and cobalt, the filtrate was treated with H_2SO_4-HNO_3 to destroy the organic matter. Thallium was estimated as Tl_2CrO_4, copper was estimated volumetrically with sodium thiosulphate and cobalt as the pyridine complex. In the case of nickel, the metal was directly estimated as the dimethylglyoxime complex.

25–47 mg of palladium could be separated from 92–116 mg of thallium or 40–51 mg of copper. 25–58 mg of palladium could be separated from 19–35 mg of cobalt or 16–20 mg of nickel. The metals were recovered with an accuracy of:

Pd 0.0 to −0.27% and Tl 0.0 to −0.16%;
Pd 0.0 to −0.28%, Cu + 0.25 to −0.37%,
Co +0.04 to −0.16%, and Ni 0.0 to −0.15%

SUMMARY

It has been shown that 1% dimethylglyoxime solution in alcohol can be efficiently used to separate quantitatively palladium from other metals of the copper group, as indicated in the new and more comprehensive scheme of qualitative analysis.

RÉSUMÉ

Une solution de diméthylglyoxime à 1% dans l'alcool peut être utilisée pour effectuer la séparation quantitative du palladium d'avec d'autres métaux du groupe du cuivre.

ZUSAMMENFASSUNG

Eine 1%ige alkoholische Lösung von Dimethylglyoxim kann zur quantitativen Abtrennung des Palladiums von den Metallen der Kupfergruppe verwendet werden.

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HIGH FREQUENCY TITRATIONS

I. THE SILVER-THIOCYANATE REACTION

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High frequency (oscillometric) methods are particularly useful for measuring the dielectric strength of a system and for detecting the end-point in a titration. By far the most ingenious application of oscillometry has been the direct determination of percentage composition of two-component single-phase mixtures by employing the use of standard curves[1]. WEST *et al.*[2-4] illustrated this procedure by the analysis of a water-benzene-methyl ethyl ketone system. They further employed the high frequency technique for the determination of small amounts of water in oils and various organic liquids. HARA AND WEST[5] used the high frequency instrument for studying the EDTA chelation of several metal ions and for the determination of organic functional groups such as imine, amine, oxime and carboxyl, both in aqueous and nonaqueous solutions. BLAEDEL AND MALMSTADT[6] demonstrated the general suitability of high frequency titrimeters for acid-base, precipitation, soluble complex formation and redox reactions. The end points were at times found to be superior to the conventional electrometric end-points. The chief advantage of all these procedures is the isolation of the system from electrodes and other active parts of the instrument without impairing their response to slight changes in the composition of the system.

The purpose of the present work was to investigate with the aid of a high frequency instrument the reactions involving the precipitation or soluble complex formation of simple and complex metal thiocyanates, and to assess the accuracy of the method for analysis of mg quantities of material in highly dilute solutions. Data presented in this communication refer to a study of the silver-thiocyanate precipitation reaction.

EXPERIMENTAL

Apparatus

A Sargent model V Oscillometer, operating at 110-120 V and 60 cycles, was used in the present series of experiments. High frequency titrations were carried out in the large 100-ml cell.

Reagents

One-tenth molar aqueous solutions of reagent-grade silver nitrate, ammonium thiocyanate, and potassium thiocyanate were prepared and standardized by the usual methods.

Procedure

Prior to its use, the oscillometer was thermally equilibriated for 30-60 min. The clean dry cell was placed in position and the needle pointer adjusted to center zero scale position. A measured volume of silver nitrate solution was transferred into the cell and the total volume brought to 100 ml with water. After the initial instrument (capacitance) reading was taken, small increments

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of ammonium or potassium thiocyanate solution were added from the buret. After each addition of the reagent, the system was stirred by means of a thin glass rod. As far as possible, the time and method of stirring were duplicated. The titration was continued beyond the stoichiometric end-point and the experimental value obtained by plotting a graph. The same procedure was adopted for reverse titrations *viz.*, thiocyanate ion against silver nitrate.

Typical curves are shown in Figs. 1–4 and representative data for silver estimation are compiled in Table I.

TABLE I

HIGH FREQUENCY TITRIMETRIC DETERMINATION OF SILVER WITH THIOCYANATE

Final molarity of $AgNO_3$ solution, M	*Silver (mg)*		*Diff. (mg)*
	actual	*found*	
1/1613	6.703	6.505	0.198
1/1336	8.082	7.842	0.240
1/2672	4.016	4.056	0.040
1/3343	3.232	3.393	0.161

DISCUSSION

During the course of a straight or a reverse titration, the instrument (capacitance) reading remains initially almost constant (*cf.* Figs. 1–4) and then rises steadily. The end-point is located at the intersection of the two straight lines. Since the initial level of the solution is above (about 1 cm) the upper edge of the electrodes, dilution effects will be negligible, the more so as the present work concerns conducting samples[1]. Furthermore, the concentration of the reagent has been adjusted in such manner that the total change in volume after titration does not exceed 3% of the original. This

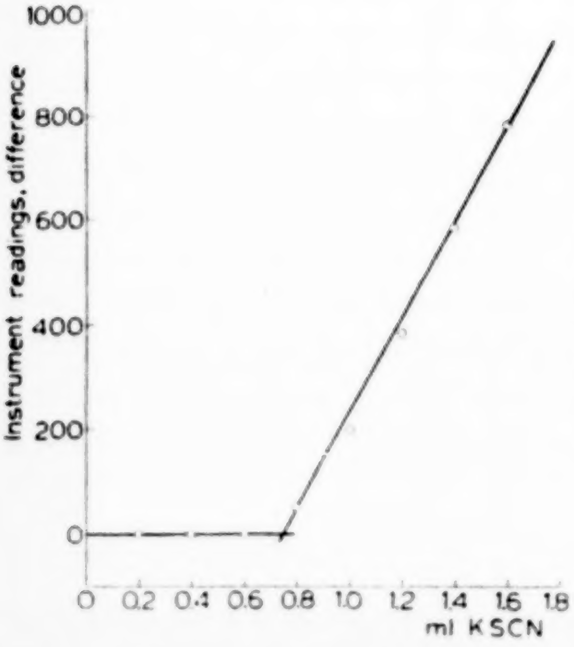

Fig. 1. Titration of $1/2672M$ $AgNO_3$ with $1/20M$ KSCN. End-point: theory: 0.745 ml; from graph: 0.75 ml.

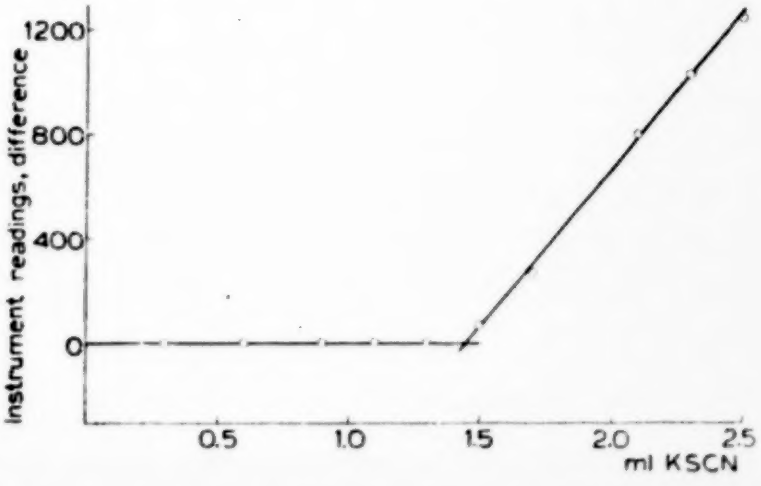

Fig. 2. Titration of $1/1336M$ $AgNO_3$ with $1/20M$ KSCN. End-point: theory: 1.49 ml; from graph: 1.45 ml.

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is easily accomplished by starting with solutions of approximately equal strength and diluting with water in the titration vessel (*cf.* EXPERIMENTAL). The silver nitrate or thiocyanate solution up to 1/4000*M* could be titrated within a maximum deviation of about 5%. At still greater dilutions, the changes in the instrument reading result in a rather flat curve making it diffucult to obtain a clear end-point. The principal advantage of the present method is that comparatively large volumes can be handled and mg quantities of silver or thiocyanate can be determined at dilutions at which the indicator or other conventional electrometric methods do not usually yield satisfactory results.

Further work on the high frequency study of mercuric thiocyanate and zinc tetracyanatomercuriate(II) is in progress.

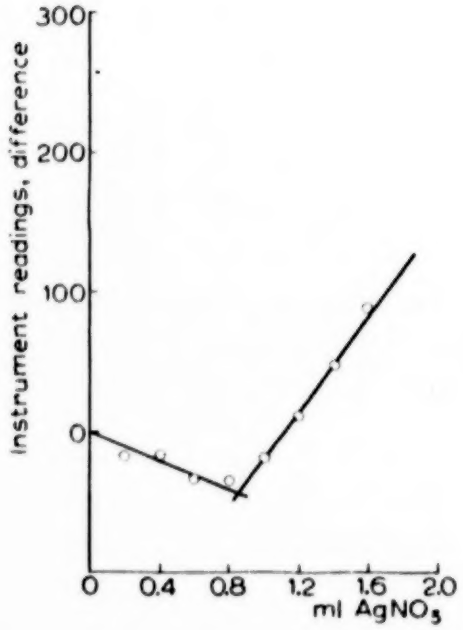

Fig. 3. Titration of 1/3982*M* KSCN with 1/33.4M $AgNO_3$. End-point: theory: 0.833 ml; from graph: 0.86 ml.

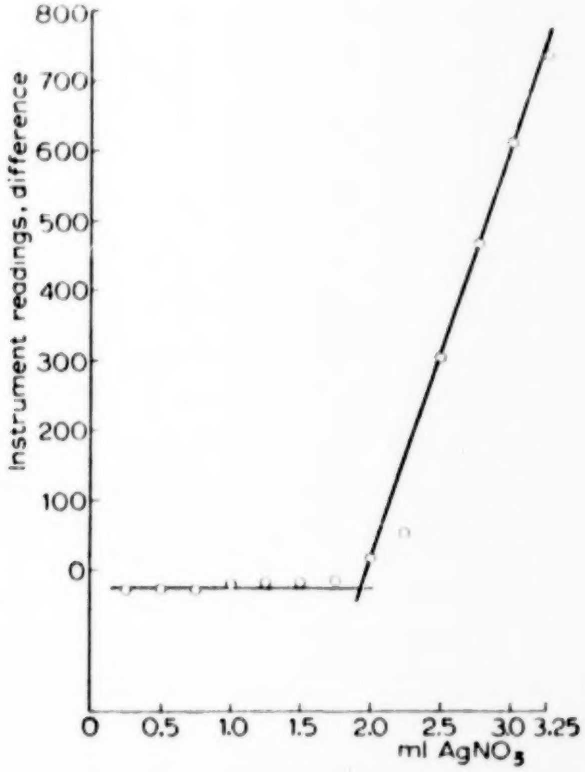

Fig. 4. Titration of 1/1680*M* NH_4SCN with 1/33.4*M* $AgNO_3$. End-point: theory: 1.983 ml; from graph: 1.925 ml.

ACKNOWLEDGEMENTS

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SUMMARY

A high frequency (oscillometric) method for the titrimetric determination of small amounts of silver at dilutions down to 1/4000*M* with ammonium or potassium thiocyanate is described. Reverse titrations in the same order of dilution are also feasible. Oscillometric studies on the formation of soluble mercuric thiocyanate and of the sparingly soluble zinc tetracyanatomercuriate(II) are in progress.

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RÉSUMÉ

Une méthode à haute fréquence (oscillométrique) est proposée pour le dosage titrimétrique de faibles teneurs d'argent, au moyen de thiocyanate d'ammonium ou de potassium.

ZUSAMMENFASSUNG

Es wird eine Hochfrequenzmethode (oszillometrisch) zur titrimetrischen Bestimmung von sehr geringen Mengen von Silber mit Ammonium oder Kaliumthiocyanatlösung beschrieben.

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THE REDUCTION OF MICRO AND SEMIMICRO WEIGHINGS TO A NORMAL TEMPERATURE AND A NORMAL PRESSURE

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As long ago as 1936[1,2] we pointed out that the accuracy of micro and semimicro weighings can be considerably increased by always reducing the balance readings to the same — but arbitrary — normal values of temperature and atmospheric pressure. The problem is essentially very simple. We know that in gravimetric determinations the correction for the buoyancy of the air for the precipitate itself is generally negligible, *viz.* in the neighbourhood of 0.1%. The buoyancy for the receptacle — crucible, weighing bottle, absorption tube, etc. — is of course far greater if expressed in % of the amount of precipitate weighed, but it is generally taken for granted that this is of no importance since the upward force on the receptacle is the same for the empty as for the full crucible. Now it is evident that this only holds good so long as the density of the air has not changed in the mean time because of changes in temperature and atmospheric pressure (and even relative humidity); and a very simple calculation shows that this can easily lead to quite considerable errors, particularly with micro and semi-micro weighings, where as a rule the ratio, weight of the receptacle : weight of the precipitate, etc., is so much more unfavourable than with macro procedures.

Example: Weight semimicro glass filtertube 7.5 g. Density of the air 1.205 mg/cm^3. Sp. gr. glass 2.5. Sp. gr. brass weights 8.4. Volume filtertube 3.0 cm^3. Volume weights 0.9 cm^3. Resulting buoyancy: (3.0–0.9) 1.205 = 2.52 mg. Therefore, if we want to weigh the precipitate exactly to 0.01 mg (semimicro), this resulting buoyancy must not change more than 0.01 mg, that is about 0.4% of its value. This implies that between the two weighings the density of the air must not change more than 0.4%. Conclusion: Changes of the atmospheric pressure of $0.004 \times 760 = 3$ mm, and changes of the temperature of $0.004 \times 293 = 1.2°$ are inadmissible!

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For micro weighings in six decimal places the limits are even about ten times narrower. Changes of 50–60 μg from one day to the next are no exceptions. To carry out the weighings in a room at a constant temperature is certainly feasible and even to be recommended. But a weighing room so completely air-conditioned that even the pressure remains constant, is hardly within the limits of practicability. Thus the evident solution of the problem is to reduce all weighings to an arbitrary normal temperature and a normal pressure. Of course this can be done by reading the temperature and the barometric pressure and calculating the desired correction. However, even when nomographs are used for this purpose, it takes so much time that hardly anybody ever does it.

There is indeed a simpler way. The buoyancy is determined by the difference in volume between the receptacle and the weights, and by the density of the air. The first factor can easily be calculated, for semimicro weighings in one's head in whole cm^3, for micro weighings with weights and specific gravities to one decimal place. So the only datum we need is the density of the air, or rather the deviation of this density from that under the chosen normal conditions. Apparatus exist from which this value can be read directly with great accuracy (Lux, Stock, Aston balance, etc.) but they are rather expensive and fragile.

For our purpose, where considerably less accuracy is required, we described[1,2] an apparatus, consisting of a barometer tube into the vacuum space of which a liquid had been brought (55 vol. % toluene, 45 vol. % benzene), which fulfils the requirement that 1 % increase of the absolute temperature increases its vapour pressure by 7.60 mm (*i.e.* 1 % of the normal atmospheric pressure). The readings of the lower mercury level are then a direct measure of changes in the density of the air.

This apparatus has rendered us excellent service in the course of the last twenty years. It considerably improved the accuracy of our micro and semimicro gravimetric determinations. However it had one very serious drawback: it was difficult to transport and therefore quite unattractive for manufacturers of laboratory instruments.

When devising means to improve it in this respect, we came to the conclusion that from the very beginning we had been on the wrong road. It is not necessary at all to make use of a true barometer tube with a vacuum at the top. A quite simple apparatus as shown in Fig. 1 will do just as well. It consists of two connecting tubes, one, A, wide and closed, the other, B, narrow and open, partly filled with mercury. The stopcocks C and D have no other use than to facilitate transport. When the apparatus is in use both should be open.

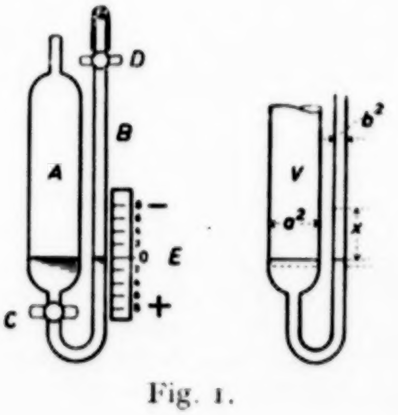

Fig. 1.

We can now bring a scale at E, divided in such a way that it shows with how many units of the fifth decimal place (0.01 mg) the weight found must be increased per cm^3 difference in volume between the receptacle and the weights, in order to reduce it to 760 mm Hg and 20°. The calculation of the length of one scale division is quite easy when the dimensions of the tubes are known.

Let us assume that in the initial state both mercury levels are at the same height. Let V (in mm^3) be the volume of the enclosed air at 760 mm and 20°, a^2 (in mm^2) the cross surface of the wide tube, b^2 (in mm^2) the same for the narrow tube; the density of the air at 760 mm and 20° is 1.205 mg/cm^3. Then we know that for a decrease of the atmospheric pressure of 1%, *i.e.* 7.60 mm, the density of the air also decreases by 1%; buoyancy per cm^3 difference in volume is also decreased by 1% of 1.205 mg per cm^3, *i.e.* 0.01205 mg. Hence for a decrease of atmospheric pressure of

$$7.60\,\frac{0.01}{0.01205} = 6.33 \text{ mm},$$

the buoyancy is decreased by 0.0100 mg. The only calculation we have to make is how much (x mm) the mercury in tube B rises, when the atmospheric pressure changes from 760 to 760—6.33 mm Hg at a constant temperature of 20°. The value of x we found is the length of one scale division.

It is evident that x is given by the formula:

$$760\,V = \left[760 - 6.33 + x\left(1 + \frac{b^2}{a^2}\right)\right]\left[V + xb^2\right]$$

in which V = volume enclosed air in mm^3 at 760 mm and 20°;
a^2 = cross surface of the wide tube in mm^2;
b^2 = cross surface of the narrow tube in mm^2.

In exactly the same way the value of x must be known for an increase of temperature equal to $\frac{0.01}{0.01205}\cdot 2.93 = 2.43°$ at a constant atmospheric pressure. In this case the formula for x is

$$\frac{760\,V}{293} = \frac{\left[760 + x\left(1 + \frac{b^2}{a^2}\right)\right]\left[V + xb^2\right]}{293 + 2.43}$$

It is easy to see that both formulas give practically the same value for x, and this is exactly why the changes in the mercury level in tube B are proportional to the changes in the density of the air.

In our first apparatus V was 22700 mm^3, a^2 199 mm^2 and b^2 14.9 mm^2. From the two formulas we found x = 4.02 mm.

A decrease of atmospheric pressure (or an increase of temperature) means a decrease of the density of the air, *i.e.* a decrease of the buoyancy. Hence the weight we find is higher than that found under normal conditions. This means that the correction we have to apply is negative. Therefore the negative readings of the scale are above the zero mark, the positive readings below it.

SUMMARY

An apparatus is described, essentially simpler than the one previously described by the author, which makes it possible to reduce all micro and semimicro weighings to a normal atmospheric pressure and a normal temperature.

RÉSUMÉ

L'auteur décrit un appareil simple permettant de ramener toutes les micro- et semimicropesées à une pression et à une température normale.

ZUSAMMENFASSUNG

Es wird ein einfacher Apparat zur Reduzierung von Halbmikro- und Mikrowägungen auf einen Normaldruck und eine Normaltemperatur beschrieben.

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NEUES VERFAHREN ZUR BESTIMMUNG DER ACETYLGRUPPE

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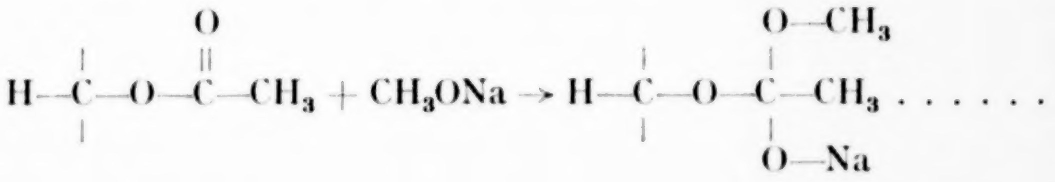
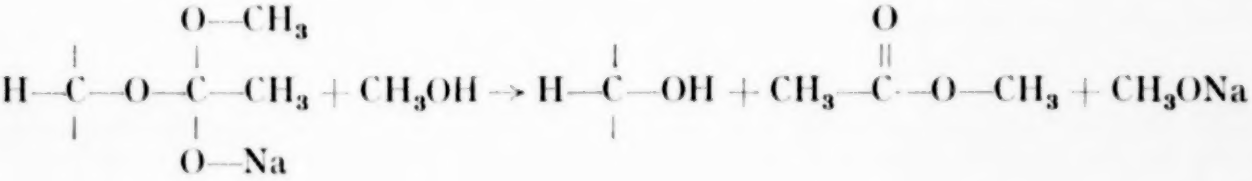
Das Wesen der sowohl in Makro- als auch in Semimikro- und Mikromengen durchgeführten und am häufigsten angewandten Verfahren zur Bestimmung der Acetylgruppe besteht in Verseifung mit Hilfe von Säure oder Lauge, Freisetzung der Essigsäure und deren Trennung durch Destillation, und schliesslich in der acidimetrischen oder jodometrischen Bestimmung der gewonnenen Essigsäure. Die Fehler dieses Verfahrens sind dem Analytiker wohl bekannt, da die Methode nicht nur langwierig, sondern in Mikromengen auch ungenau ist. Es zeigen sich ausserdem Schwierigkeiten nicht nur in der Auswahl des geeignetesten Verseifungsmittels, sondern auch zufolge jenes Umstandes, dass die Verseifung in heterogener Phase nicht vor sich geht, sondern nur im Falle solcher Verbindungen zustandekommt, die in Wasser, Säure oder Lauge bzw. Alkohol löslich sind. Andere Verfahren, wie z.B. jenes, bei welchem die Verseifung in acetonhaltiger Lösung mit überschüssiger Lauge vorgenommen und der Laugeüberschuss rücktitriert wird[1,2], oder ein anderes, bei welchem die Verseifung in Anwesenheit von Äthylalkohol mit *p*-Toluolsulfonsäure durchgeführt und das gewonnene Äthylacetat abdestilliert wird[3,4], können nur zur Analyse einiger, über O-Acetylbindung verfügender Verbindungen herangezogen werden.

ZEMPLÉN und Mitarbeiter[5-7] entwarfen eine präparative Methode für die Herstellung desacetylierter Kohlenhydraten, bei welcher die acetylierten Kohlenhydrate in absoluter methyl-alkoholischer Lösung mit Natriummethylat reagierten und auf diese Weise im ersten Schritt das Natriumsalz des Essigsäurediesters entstand:



$$H-\underset{|}{\overset{|}{C}}-O-\overset{\overset{O}{\|}}{C}-CH_3 + CH_3ONa \rightarrow H-\underset{|}{\overset{|}{C}}-O-\underset{\underset{O-Na}{|}}{\overset{\overset{O-CH_3}{|}}{C}}-CH_3 \;\ldots\ldots\; (I)$$

Dieses setzte sich auf Einwirkung von Methylalkohol zu Kohlenhydrat und Methylacetat um, wobei sich das Natriummethylat regenerierte:



$$H-\underset{|}{\overset{|}{C}}-O-\underset{\underset{O-Na}{|}}{\overset{\overset{O-CH_3}{|}}{C}}-CH_3 + CH_3OH \rightarrow H-\underset{|}{\overset{|}{C}}-OH + CH_3-\overset{\overset{O}{\|}}{C}-O-CH_3 + CH_3ONa \quad (II)$$

ZEMPLÉN und Mitarbeiter stellten dabei fest, dass das Natriummethylat den Vorgang katalysiert.

Im Laufe unserer Untersuchungen fanden wir, dass diese Reaktion nicht nur zur

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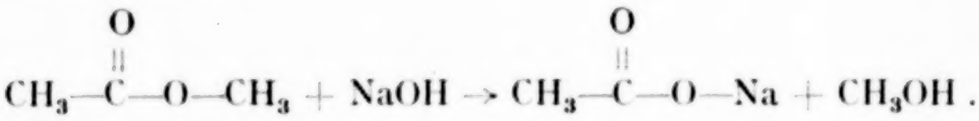
Desacetylierung von Kohlenhydraten geeignet ist, sondern dass mit Natriummethylat auch andere Verbindungen reagieren, falls die Acetylgruppe durch ein Sauerstoffatom an das Molekül gebunden ist. Dieses Reaktionsprinzip schien also zur schnellen und einfachen Bestimmung der Acetylgruppe mit Hilfe des im Laufe der Reaktion entstehenden Methylacetats geeignet zu sein.

Wird nämlich das an Reaktionen (I) und (II) beteiligte Natriummethylat mit Wasser zersetzt, so entstehen Methylalkohol und Natriumhydroxyd in der zum Gleichgewicht führenden, doch stark nach rechts verschobener Reaktion:

$$CH_3ONa + H_2O \rightarrow CH_3OH + NaOH \quad \ldots\ldots\ldots \quad (III)$$

Das Natriumhydroxyd verseift sodann das Methylacetat, wodurch Natriumacetat und Methylalkohol entstehen:



$$CH_3\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}O\text{—}CH_3 + NaOH \rightarrow CH_3\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}O\text{—}Na + CH_3OH \quad \ldots\ldots \quad (IV)$$

Da wir aber das Kaliummethylat wirkungsvoller fanden als das Natriummethylat, benützten wir im weiteren ausschliesslich Kaliummethylat zu unseren Versuchen.

Nach Beendigung der Reaktionen (I) und (II) zersetzt sich das Kaliummethylat also quantitativ laut Reaktion(III). Wird jedoch das Kaliummethylat als Masslösung in überschüssiger Menge angewandt, so wird das daraus entstandene Kaliumhydroxyd nicht vollständig in der Reaktion(IV) verbraucht; die überschüssige Menge lässt sich mit Säure rücktitrieren. Kennt man den Wirkungswert der Kaliummethylatlösung, d.h. die Menge des aus ihr durch Hydrolyse freisetzbaren Kaliumhydroxyds und bestimmt man die Menge des nach der Reaktion zurückgebliebenen Kaliumhydroxyds, so ist die Differenz der beiden Bestimmungsergebnissen mit dem aus der Verbindung gebildeten Methylacetat, folglich mit der Acetylgruppe äquivalent. Voraussetzungen sind dabei jedoch der vollständige Ablauf der Desacetylierung und der Hydrolyse, weiterhin, dass das Kaliummethylat bzw. das daraus entstehende Kaliumhydroxyd ausschliesslich auf Einwirkung der Acetylgruppe eine Änderung erleiden, und dass keine andere Nebenreaktionen sich abspielen.

Bezüglich der Brauchbarkeit des Verfahrens ist also die Stabilität der Kaliummethylatlösung entscheidend und zwar nicht nur bei Zimmertemperatur, sondern auch bei Siedetemperatur. Es wurde gefunden, dass der Wirkungswert, falls die Lösung in gut verschlossener Flasche aufbewahrt wurde, drei Wochen hindurch unverändert blieb. Die Lösung war titerbeständig auch bei drei Stunden langern Kochen in einem, mit Rückflusskühler versehenem Destillierkolben.

Wir bewiesen ausserdem, dass bei der Analyse von nicht-Zuckerderivaten, sondern z.B. von Triacetylcellulose oder Diacetylmorphin, die Reaktion ebenfalls durch katalytische Desacetylierung und nicht durch einfache alkalische Hydrolyse vor sich geht. Falls wir nämlich nach der Verseifung den Inhalt des Kolbens abdestillierten, fanden wir das Methylacetat quantitativ im Destillat vor. Im Falle einer einfachen alkalischen Hydrolyse hätte Natriumacetat entstehen müssen, das selbstverständlich ohne Ansäuern nicht destilliert werden kann. Die Hydrolyse vollzieht sich nicht plötzlich sondern nimmt etwa 10 min in Anspruch.

Die Bestimmung der Acetylgruppe durch direkte Titration kann jedoch nur dann erfolgen, wenn das Molekül keine saure oder basische Gruppen enthält und auch keine mit Laugenverbrauch verbundene Zersetzung zustandekommt, wie z.B. im Falle der Acetate der reduzierenden Zuckersorten. Ist die Lösung der Substanz schon ursprünglich farbig oder nimmt sie im Laufe der Desacetylierung Farbe an, so wandten wir zur Titration statt Phenolphthalein chemilumineszierende Indikatoren an. Das Lucigenin[8] bewies sich z.B. sehr dazu geeignet.

Falls aus den oben erwähnten Gründen die Titration nicht direkt auszuführen wäre, so destillieren wir das in Reaktion(II) entstandene Methylacetat in einem geschlossenem Apparat ab, und fangen das Destillat in einem mit Rückflusskühler versehenen Kolben in Laugelösung von bekannter Menge und bekanntem Titer auf. Das Methylacetat wird mit Lauge hydrolysiert und der Laugenüberschuss wird sodann titriert. Um den raschen und quantitativen Verlauf der Reaktion zu befördern, wird in solchen Fällen zur Desacetylierung 1 N Kaliummethylatlösung im Überschuss angewandt.

Diese letztere modifizierte Form des Verfahrens führt im Falle sämtlicher Verbindungen des O-Acetyl Types zu genauen Ergebnissen, mit Ausnahme jener Verbindungen, bei denen im Laufe der Desacetylierung destillierbare Säure oder Lauge als Zerfallsprodukt zustandekommt. Beide modifizierte Formen des Verfahrens liefern einwandfreie Ergebnisse, sogar wenn die Verbindung in Methylalkohol unlöslich ist. Die Desacetylierung geht daher auch in heterogener Phase mit genügender Geschwindigkeit und quantitativ vor sich.

Mit Hilfe direkter Titration bestimmten wir die Acetylgruppengehalt von Oktaacetylsaccharose, Pregnenolonacetat, Triacetylcellulose, 3α-Acetoxy-5β-ergost-22-en, Diacetylmorphin und β-Naphtholacetat. Substanzmengen von 45–300 mg wurden mit 10 ml 0.1 N Kaliummethylatlösung desacetyliert. Bei der Rücktitration des überschüssigen Natriumhydroxyds ergab sich der Verbrauch an 0.1 N Salzsäurelösung zu 0.73–7.7 ml. Die in Prozentsatz ausgedrückte Abweichung vom theoretischen Acetylgruppengehalt bewegte sich zwischen + 0,41 und — 0.41 %.

Bei der Titration von β-Naphtholacetat wurde als Indikator Lucigenin angewandt.

Zu indirekter, nach Destillation erfolgender Bestimmung des Acetylgruppengehalts wurden folgende Substanzen herangezogen: Pentaacetyl-D-glucose, Oktaacetylcellobiose, Oktaacetylsaccharose, β-Naphtholacetat, 3α-Acetoxy-5β-ergost-22-en, Diacetylmorphin, Triacetylcellulose und Polyvinylacetat. In 5–8 Parallelversuchen wurden Substanzmengen von 39.2–184.0 mg eingewogen und das Methylacetat-Destillat wurde im Rezipienten in 10.0 ml 0.1 N NaOH-Lösung aufgefangen. Bei der Rücktitration bewegte sich der Verbrauch an 0.1 N HCl zwischen 1.66 und 7.89 ml. Die in Prozentsatz ausgedrückte Abweichung vom theoretischen Wert bewegte sich zwischen — 0.44 und + 0.52 %.

DANK

Herrn Prof. ERDEY, der unsere Arbeit von Anfang an verfolgte und durch seine wertvollen Ratschläge beförderte sprechen wir hiermit unseren Dank aus.

ZUSAMMENFASSUNG

Der O-Acetylgruppenhalt organischer Verbindungen kann einfach und genau bestimmt werden, indem in abs. methylalkoholhaltiger Lösung oder Suspension mit bekannter Menge einer Kaliummethylatlösung verseift und danach das nichtverbrauchte Kaliummethylat nach Hydrolyse als Kaliumhydroxyd titriert wird. Als Indikator dient Phenolphthalein, oder, falls die Lösung farbig ist, Lucigenin. Ist die Titration in der Lösung nicht direkt ausführbar, so wird das bei der Verseifung entstehende Methylacetat abdestilliert, in Laugenlösung aufgefangen und der Laugenüberschuss nach Hydrolyse rücktitriert.

Das Verfahren wurde mit gutem Erfolg bei Acetylbestimmungen in reduzierenden und nichtreduzierenden Zuckeracetaten, Celluloseacetaten, Polyvinylacetaten, β-Naphtholacetat, Pregnenolonacetat, 3α-Acetoxy-5β-ergost-22-en, weiterhin in Diacetylmorphin erprobt. Ein Vorteil des Verfahrens gegenüber den bekannten Methoden ist seine schnelle Ausführbarkeit und der Umstand, dass die Verseifung sich auch in heterogener Phase vollzieht.

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SUMMARY

A simple and accurate method is described for the determination of acetyl groups in various organic compounds. The compound is dissolved or suspended in absolute methanol and saponified with a known quantity of potassium methylate solution. The excess potassium methylate is then hydrolysed and determined as potassium hydroxide by titration, an appropriate indicator being used.

RÉSUMÉ

Une méthode pour le dosage du groupement acétyle dans divers composés organiques est proposé. On traite la solution, ou la suspension, à analyser par une solution de méthylate de potassium, dont l'excès est ensuite hydrolysé en hydroxyde de potassium, que l'on titre en présence d'un indicateur approprié.

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METOMEGA CHROME CYANINE BLL AS A METAL INDICATOR IN EDTA TITRATIONS

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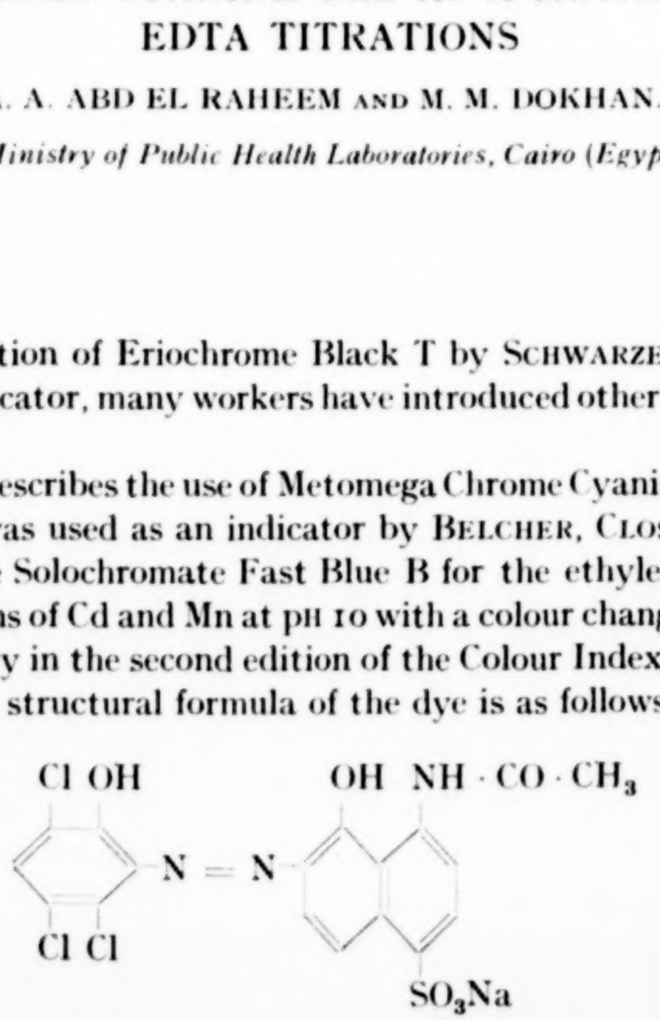
Since the introduction of Eriochrome Black T by SCHWARZENBACH AND BIEDERMANN[1] as a metal indicator, many workers have introduced other azo dyes for the same purpose.

The present work describes the use of Metomega Chrome Cyanine BLL for analytical purposes. This dye was used as an indicator by BELCHER, CLOSE AND WEST[2] under the I.C.I. trade name Solochromate Fast Blue B for the ethylenediaminetetraacetic acid (EDTA) titrations of Cd and Mn at pH 10 with a colour change from purple to red. According to the entry in the second edition of the Colour Index[3], it is known as C. I. Mordant Blue 7. The structural formula of the dye is as follows:



Properties of Metomega Chrome Cyanine BLL

Cyanine BLL is a blue-black powder with a faint metallic lustre, soluble in water and ethanol giving a sky-blue solution. The colour of the dye is very sensitive to pH variations. In the pH range from 5.7 to 7.9 the dye solution is blue, while it changes to violet at higher or lower pH ranges. Thus it seems that Cyanine BLL will find no application in highly acedic or alkaline pH ranges. The aqueous and ethanolic solutions of the dye are stable for a few days; however, if the solution is kept for a period of more than a week the colour gradually changes and after about 10 days it turns completely to brown-red because of polymerisation.

Cyanine BLL metal complexes

The metal complexes of Cyanine BLL are readily prepared by adding a few drops of a freshly prepared aqueous solution of the dye to solutions of heavy metals. The results obtained indicated that red chelate compounds were formed, regardless of the nature of the anion present, when the pH of the solution was maintained within the range 5.7 to 7.9. The cations that caused a colour change are listed in Table I.

TABLE I

COLOUR REACTIONS AND SENSITIVITY LIMITS OF METALLIC IONS WITH CYANINE BLL

Ion	*Colour*	*Identification limit µg*	*Dilution limit*
Al	pink	0.22	$1:1.36\cdot10^5$
Ba	pink		
Ca	wine red	0.20	$1:1.5\cdot10^5$
Cd	red	0.56	$1:5.3\cdot10^4$
Co	red	0.12	$1:2.5\cdot10^5$
Cu	red	0.13	$1:2.3\cdot10^5$
Fe^{+3}	pink	0.17	$1:1.8\cdot10^5$
Pb	wine red	2.07	$1:1.4\cdot10^4$
Mn	wine red	0.33	$1:9\cdot10^4$
Hg	red	1.40	$1:2.1\cdot10^4$
Ni	wine red	0.18	$1:1.7\cdot10^5$
Sr	pink		
Th	pink	0.71	$1:4.3\cdot10^5$
U	pink	0.71	$1:4.2\cdot10^4$
Zn	wine red	0.13	$1:2.3\cdot10^5$
Zr	wine red	1.37	$1:2.1\cdot10^4$

Spot tests were performed by mixing a micro drop (0.03 ml) of the metal solution with a micro drop of an aqueous 1% solution of the dye at pH 6.8. These tests were also carried out with a solution of known concentration of the metal ion. Solutions with lower concentrations were prepared by progressive dilution and were tested in the same manner. A blank experiment was carried out for comparison. In this way the detection limits of the cations were estimated and the corresponding dilution limits were computed.

Results and remarks on spot tests

The results in Table I show that the blue colour of Cyanine BLL turns to pink or wine red on the addition of the ions indicated in Table I.

From the sensitivity limits of the reactions causing colour change it can be seen that the presence of Al^{+3}, Ca^{+2}, Cd^{+2}, Co^{+2}, Cu^{+2}, Fe^{+3}, Pb^{+2}, Mn^{+2}, Hg^{+2}, Ni^{+2}, Th^{+4}, U^{+4}, Zn^{+2}, and Zr^{+4} can easily be detected when small amounts of these ions are present in solutions and that the reaction may be applied for the detection of the end-points of titrations of these metals with EDTA.

APPLICATIONS

The use of Cyanine BLL as a metal indicator in EDTA titrations has been investigated. The results obtained show that the indicator is particularly suitable for the titration of Zn^{+2}, Cd^{+2}, Mn^{+2} and Pb^{+2} because of the reversibility and sensitivity of the colour change of the indicator. Copper gave a reversible colour change with the dye but the amounts of EDTA required are much more than the equivalent amounts. Ba^{+2}, Ca^{+2}, Mg^{+2}, and Sr^{+2} gave weak complexes with the dye. The rest of the metals gave an irreversible colour change.

Reagents

Indicator powder: 0.1 g of Metomega Chrome Cyanine BLL (Sandoz) was ground with 10 g of sodium chloride (A.R.).

EDTA solution 0.01*M*: Dissolve 3.722 g of reagent grade disodium ethylenediaminetetraacetate dihydrate in water; dilute to 1 l with bidistilled water.

Buffer solution (pH 6.8): Mix 522 ml of 0.1*M* sodium diethylbarbiturate with 478 ml of 0.1*N* HCl.

Metal salt solution: Prepare 0.01*M* solutions of the various metals from analytical grade reagents. Standardize these solutions against EDTA using Eriochrome Black T or murexide as indicator according to the usual procedure for the determination of the appropriate cation.

Other reagents: Ascorbic acid, Eriochrome Black T indicator powder.

Procedure for the determination of Zn, Cd, Mn and Pb

To an aliquot portion of the sample solution in a conical flask, add 5 ml of the buffer and a few mg of the indicator until the solution becomes clearly coloured red or pink. When of determining manganese add a few crystals of ascorbic acid. Titrate with 0.01*M* EDTA until the colour changes to clear blue.

1 ml of the titrant corresponds to 653.8 μg of Zn, 1124.1 μg of Cd, 549.4 μg of Mn or 2072.1 μg of Pb.

Results and remarks

The results given in Table II show the slight differences between the amounts of zinc taken and found, as well as the calculated volume of EDTA required and that consumed in titrations. These data are those of representative samples of a large number of determinations, the calculated standard deviation was found to be 7.0 μg and therefore the probable error was 4.6 μg when 0.01*M* EDTA solution was used. Similar data are shown in Table II for the determination of cadmium, manganese, and lead. The standard deviations and probable errors of determination of these metals were 12.5 μg and 8.1 μg for cadmium; 8.1 μg and 5.4 μg for Mn; and 19.5 μg and 13 μg for lead.

The end-points of titrations of zinc, cadmium, manganese and lead were very sharp and could be easily detected. It is therefore concluded that Metomega Chrome Cyanine BLL is a suitable indicator for the titration of these metals.

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TABLE II

EDTA TITRATIONS OF SOME METALS USING CYANINE BLL AS INDICATOR

Metal ion	*mg metal*			*ml 0.01 M EDTA*		
	present	*found*	*error*	*calculated*	*consumed*	*error*
Zn	0.968	0.968	0.00	1.48	1.48	0.00
	1.412	1.406	0.006	2.16	2.15	0.01
	2.066	2.079	0.013	3.16	3.18	0.02
	3.530	3.530	0.00	4.14	4.14	0.00
Cd	1.124	1.124	0.00	1.00	1.00	0.00
	2.068	2.057	0.011	1.84	1.83	0.01
	3.182	3.200	0.023	2.92	2.94	0.02
	4.541	4.563	0.022	4.04	4.06	0.02
	6.362	6.396	0.034	5.66	5.69	0.02
Mn	1.099	1.109	0.010	2.00	2.02	0.02
	1.318	1.301	0.017	2.4	2.37	0.03
	2.560	2.565	0.005	4.66	4.67	0.01
	3.457	3.457	0.00	6.22	6.22	0.00
Pb	1.202	1.243	0.041	0.58	0.60	0.02
	3.067	3.067	0.00	1.48	1.48	0.00
	11.272	11.334	0.062	5.44	5.47	0.03
	13.717	13.759	0.042	6.62	6.64	0.02

SUMMARY

A study was made of the suitability of Metomega Chrome Cyanine BLL as a metal indicator for the EDTA titration of zinc, cadmium, manganese and lead. Spot tests for the determination of the sensitivity limits are described.

RÉSUMÉ

Le ,,Metomega Chrome Cyanine BLL'' est proposé comme indicateur pour le titrage du zinc, du cadmium, du manganèse et du plomb, au moyen d'EDTA. Les limites de sensibilité des réactions de ce réactif avec divers cations ont été déterminées.

ZUSAMMENFASSUNG

,,Metomega Chrome Cyanin BLL'' wird als Metall-Indikator für die EDTA Titration von Zink, Cadmium, Mangan und Blei vorgeschlagen. Die Empfindlichkeit des Indikators gegenüber den einzelnen Kationen wurde mit Hilfe von Tüpfelproben bestimmt.

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A QUALITATIVE AND QUANTITATIVE COLOR REACTION FOR PYRIDOXAL WITH SULFURIC ACID*

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INTRODUCTION

Many color reactions utilized qualitatively and quantitatively in biological chemistry are based upon the aldehyde-phenol-acid reaction system. One component of this system may be determined if the reagents furnish the other two components. The aldehyde and the phenol condense to form a chromogenic complex in the presence of a condensing agent such as concentrated hydrochloric or sulfuric acid[1-3].

The aldehyde-phenol-acid reaction system has furnished analytical procedures for a large variety of compounds:

1. Phenols
2. Phenologenic compounds, such as quinones, which on reduction produce phenols.
3. Aldehydes
4. Aldehydogenic compounds, among which may be mentioned the following compounds:
    (a) Primary alcohols, which yield aldehydes on oxidation.
    (b) Carbohydrates, which in themselves contain a free or combined aldehyde group, and which on treatment with hydrochloric acid or sulfuric acid of sufficient concentration, disrupt to form the aldehyde, furfural or its derivatives, methylfurfural and hydroxymethylfurfural.
    (c) Glycol, glycerol, and higher polyalcohols, sugars, and α-amino alcohols, which yield aldehydes on oxidation with periodate (Malaprade reaction).
    (d) Amino acids, which react with ninhydrin to liberate carbon dioxide and ammonia, and to produce an aldehyde. Glycine, proline and hydroxyproline produce aldehydes with ninhydrin.
    (e) Carboxylic acids, such as citric acid, succinic acid, malic acid, tartaric acid, glycolic acid or lactic acid, which react with concentrated sulfuric acid to yield an aldehyde. Glycolic acid produces formaldehyde, and lactic acid yields acetaldehyde.
    (f) Alkaloids, such as narcotine and hydrastine, which on oxidative hydrolysis, yield the aldehyde, opianic acid (3,4-dimethoxy-*o*-aldehydo-benzoic acid.)

5. Inorganic acids, such as hydrochloric acid or sulfuric acid.

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In the aldehyde-phenol-acid reaction system a ketone may be substituted for the aldehyde, since both types of compounds possess a common group, the C=O or carbonyl group. Not only ketones and ketoses, but ketogenic compounds, such as secondary alcohols, may be determined by means of the ketone-phenol-acid reaction system. Certain sugars, such as the hexoses, in addition to forming derivatives of furfural on treatment with acid, may also produce at the same time the ketonic acid, levulinic acid, which is 3-keto-*n*-valeric acid.

As illustrations of the aldehyde-phenol-acid reaction system a few well-known analytical procedures will be cited. The *Marquis reaction* for the detection of morphine and other phenolic alkaloids requires the Marquis reagent, which is formaldehyde in sulfuric acid. Acetaldehyde is determined qualitatively or quantitatively by the characteristic coloration formed by the interaction of the phenolic compound, *p*-hydroxydiphenyl and sulfuric acid[4]. This method can be employed for the determination of paraldehyde and of lactic acid, both of which on treatment with sulfuric acid can be converted to acetaldehyde[5].

The *Molisch test* for carbohydrates uses the phenol, *α*-naphthol, in the presence of sulfuric acid. The *Günzberg test* is considered one of the most satisfactory tests for free hydrochloric acid in gastric contents. The test requires the Günzberg reagent, which contains the triphenol, phloroglucin, and the aldehyde, vanillin, in 95% alcohol. A similar test for free hydrochloric acid in gastric contents is the *procedure of Boas*. Gastric contents are evaporated together with the reagents, the diphenol, resorcinol and sucrose. In the presence of free hydrochloric acid, a rose-red color is produced. The acid hydrolyzes the sucrose to form glucose and fructose, which on further action of the acid produces the aldehyde, hydroxymethylfurfural, which may eventually yield the ketonic acid, levulinic acid.

We were attempting to develop a color reaction for pyridoxal (2-methyl-3-hydroxy-4-aldehydo-5-hydroxymethyl pyridine). This vitamin contains a phenolic hydroxyl and an aldehyde group. Pyridoxine, pyridoxamine and pyridoxic acid, contain a phenolic hydroxyl but no aldehyde group. We know that many organic compounds, such as sterols, bile acids and corticosteroids, though not phenolic aldehydes or phenolic ketones, yield reactions with more or less concentrated sulfuric acid. Nevertheless we advanced, in consideration of the carbonyl-phenol-acid reaction system, the hypothesis that an aromatic compound containing within its structure an aldehyde or ketone group as well as an hydroxyl group should yield a characteristic color reaction when the reagent consists solely of sulfuric acid. We were encouraged to advance this hypothesis when we found that certain compounds possessing both a phenol and a carbonyl group reacted with concentrated sulfuric acid. Salicylaldehyde (*o*-hydroxybenzaldehyde) yields a yellow color with concentrated sulfuric acid, while salicylic acid (*o*-hydroxybenzoic acid) does not react chromogenically with sulfuric acid. Colchicine is a phenolic ether with one ketone group. It possesses three methoxy groups which are potential phenolic hydroxyls. With concentrated sulfuric acid, colchicine develops a yellow color. Heliotropine (dihydroxymethylene protocatechuic aldehyde) and veratryl aldehyde (3,4-dimethoxybenzaldehyde) also develop yellow colors with sulfuric acid. Estrone is a phenolic ketone yielding with sulfuric acid a characteristic color reaction utilized in the quantitative estimation of this hormone[6]. The phenolic glycosides, salicin, containing the phenolic aglucon, *o*-hydroxybenzyl alcohol and phlorhizin, containing the phenolic and ketonic aglucon, *p*-dihydroxyphenyl propiophenone, yield characteristic color reactions with sulfuric acid. Salicin produces a bright red color, and phlorhizin a light yellow color changing to light orange.

If our hypothesis has any merit, anisaldehyde which is an aldehydic phenolic ether, and vanillin, which contains a phenolic hydroxyl, a methoxy group and an aldehyde group, should yield a color complex with concentrated sulfuric acid. On the other hand, anisic acid and vanillic acid, both of which contain a phenolic or phenolic ether group only should not react chromogenically with concentrated sulfuric acid. Pyridoxine is a pyridine derivative with one hydroxyl group at carbon 3. This hydroxyl group reacts like a phenolic hydroxyl. Pyridoxine reacts with ferric chloride to yield a red-brown or orange-red color[7,8]. We have found pyridoxal also to react with ferric chloride. Pyridoxine, pyridoxal and pyridoxamine have been reported to couple with diazonium compounds. Pyridoxal, which possesses both an aldehyde group and a phenolic hydroxyl, should yield a chromogenic complex with concentrated sulfuric acid. Pyridoxine, pyridoxamine and pyridoxic acid, possessing a phenolic hydroxyl but not an aldehyde group, should not yield a color reaction with sulfuric acid.

EXPERIMENTAL

The phenolic aldehydes and phenolic ketones investigated were dissolved in absolute alcohol. The alcohol was heated with silver acetate and sodium hydroxide and subsequently subjected to distillation. With one compound, *p,p'*-dimethoxybenzophenone, benzene had to be used as the solvent because the compound was insoluble in alcohol. The compounds were made up in two solutions. Solution A contained one mg/ml (0.1% by weight) and solution B, 5 mg/ml (0.5% by weight). In the case of liquid compounds, *o*-methoxybenzaldehyde, *p*-methoxybenzaldehyde (anisaldehyde), *o*-ethoxybenzaldehyde, *o*-hydroxybenzaldehyde (salicyl aldehyde)and *o*-hydroxyacetophenone, two solutions were made up, one representing 1% by volume (Solution C) and the other 5% by volume (Solution D)*. One set of experiments was designed for a zone test. For this set we employed 2 ml of each of these four solutions and 2 to 3 ml concentrated sulfuric acid. To avoid side reactions and possible charring, the tubes containing the solutions were kept in ice water before, during, and after the addition of sulfuric acid. In a second set of experiments varied quantities of the compounds in definite concentrations were mixed with 2.5 ml of concentrated sulfuric acid. The mixture was shaken to diffuse the color which developed. This set of experiments was also performed with the aid of ice water.

The phenolic aldehydes, anisaldehyde and vanillin, gave positive reactions with concentrated sulfuric acid. The phenolic acids, anisic acid and vanillic acid, yielded no color with sulfuric acid. We have also tested aesculin with concentrated sulfuric acid and found it to give a yellow color or a yellow color with a greenish tinge at higher concentrations. Aesculin is a glycoside in which the aglucon is the diphenolic compound aesculetin (6,7-dihydroxycoumarin). Aesculetin reacts with ferric chloride to yield a green color. The aesculetin furnishes the phenolic hydroxyls, while the glucose portion of the molecule on treatment with acid disrupts to produce the aldehyde, hydroxymethylfurfural, which may in turn be converted to the ketocarboxylic acid, levulinic acid. We have also investigated two phenolic glycosides, arbutin (Table I and III) and rutin (Tables II and IV).

We have tested the four compounds related to vitamin B_6 (pyridoxine, pyridoxamine, pyridoxal and pyridoxic acid). Pyridoxal hydrochloride or phosphate is the only compound that gave an intense yellow color with concentrated sulfuric acid. While

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* The liquid compound, *p,p'*-dimethoxybenzophenone, dissolved in benzene, was made up in concentrations of 1% and 5% by volume.

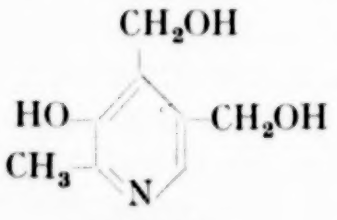
TABLE I

REACTIONS OF PHENOLIC ALDEHYDES WITH SULFURIC ACID; ZONE TESTS REACTIONS AT INTERFACE

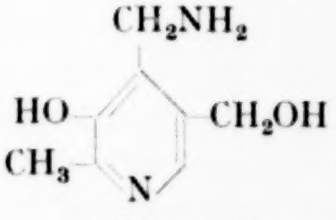
Compound	*Concentration of compound (by weight)*	
	2 ml of 1.0% solution	*2 ml of 5.0% solution*
1. *p*-Hydroxybenzaldehyde	yellow ring	yellow ring
2. Sodium-4-hydroxybenzaldehyde-3-sulfonate	yellow ring	yellow ring
3. 2-Hydroxy-5-chlorbenzaldehyde	yellow ring	deep yellow ring
4. 2-Hydroxy-5-brombenzaldehyde	yellow ring	deeper yellow ring
5. 2,4-Dihydroxybenzaldehyde	light yellow ring; very light violet above ring	yellow ring; distinct violet above ring
6. 2-Hydroxy-3-methoxybenzaldehyde	golden yellow ring	orange ring
7. 4-Hydroxy-3-ethoxybenzaldehyde	yellow ring	deep yellow ring
8. 2,3-Dimethoxybenzaldehyde	yellow orange ring	deep orange ring
9. 4-Hydroxy-3-methoxybenzaldehyde (vanillin)	deep yellow ring	deep greenish brown ring
10. Hydroquinone-glucose (arbutin)	faint yellow ring	yellowish brown ring
	Concentration of compound (by volume)	
	2 ml of 1.0% solution	*2 ml of 5.0% solution*
11. *o*-Hydroxybenzaldehyde [a] (salicylaldehyde)	reddish orange ring	deep red ring
12. *o*-Methoxybenzaldehyde [a]	purplish ring	purplish ring
13. *p*-Methoxybenzaldehyde [a] (anisaldehyde)	greenish brown ring	greenish purple ring
14. *o*-Ethoxybenzaldehyde [a]	dark reddish brown ring	dark reddish brown ring
15. 3,4-Diethoxybenzaldehyde [a]	deep reddish orange violet ring	reddish violet ring

[a] The compounds are liquids.

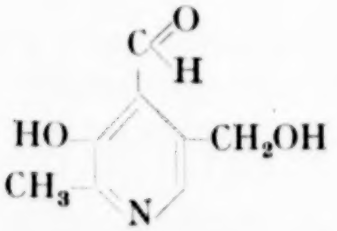
all the four compounds related to vitamin B_6 possess a phenolic hydroxyl, pyridoxal is the only one that possesses a phenolic hydroxyl as well as an aldehyde group.



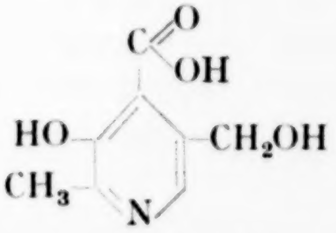
pyridoxine



pyridoxamine



pyridoxal



pyridoxic acid

TABLE II

REACTION OF PHENOLIC KETONES WITH SULFURIC ACID; ZONE TESTS REACTIONS AT INTERFACE

Compound	*Concentration of compound*	
	2 ml of 0.1% solution	*2 ml of 0.5% solution*
1. *o*-Hydroxyacetophenone [a]	yellow ring	deep yellow ring
2. *p*-Hydroxyacetophenone	no color	faint golden yellow ring
3. *p*-Hydroxypropiophenone	no color	light green and yellow rings
4. 4-(*o*-Hydroxyphenyl)-3-butene-one	orange ring	red ring
5. 2,4-Dihydroxyacetophenone (resacetophenone)	no color	light yellow ring
6. Anisalacetone	orange ring	deep orange ring
7. Vanillalacetone	orange ring	red ring
8. 4-Hydroxybenzophenone	yellowish green ring	yellowish green ring
9. 4,4′-Dihydroxybenzophenone	yellow ring	deep yellow ring
10. *p,p*′-Dimethoxybenzophenone [a]	yellow	deep yellow
11. Hydroxy-2-acetonaphthone	yellow ring	golden yellow ring
12. Quercetin [b]	yellow ring	orange ring
13. Rutin	yellow ring	yellow ring

[a] The compound is a liquid. The quantities used in the test are 2 ml of 1% and 2 ml of 5% by volume.

[b] Quercetin (pentahydroxyflavone) is a polyphenolic quinone with a C = O group at position 4 in the molecule. It crystallizes in yellow needles and gives an intense green color with ferric chloride. Rutin is a flavone glycoside, the carbohydrate rutinose, which is 6-D-glucose-β-L-rhamnoside, being linked to quercetin at carbon 3.

The color reaction with pyridoxal is sensitive to 1 μg when 2 drops of 0.5% copper sulfate are added and the reaction mixture heated on the water bath for 10 to 15 min. The color reaction is sensitive to 10 μg without the addition of copper sulfate and without the aid of heat.

QUANTITATIVE DETERMINATION

The absorption spectrum of pyridoxal hydrochloride was determined by means of the DU Beckman spectrophotometer, using 100 μg of the compound dissolved in 1 ml of distilled water and 4 ml of concentrated sulfuric acid (Mallinckrodt-A.C.S. specifications) (Fig. 1). The reaction was carried out at room temperature. The absorption

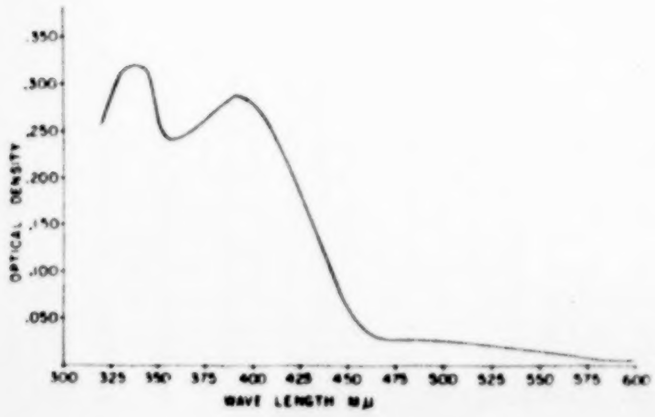


Fig. 1.

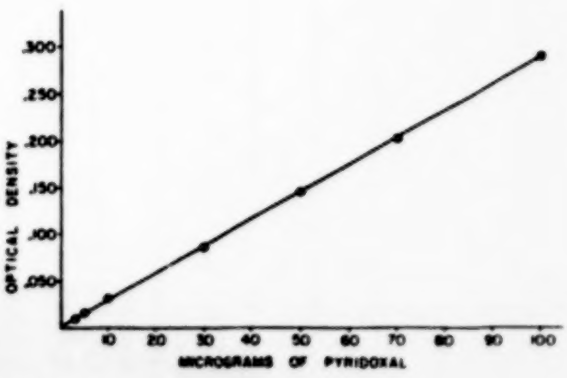


Fig. 2.

TABLE III REACTIONS OF PHENOLIC ALDEHYDES WITH SULFURIC ACID; DIFFUSION TESTS

Compound	*Concentration of compound*					
	0.1% by weight			*0.5% by weight*		
	0.2 ml	*0.5 ml*	*1.0 ml*	*1.0 ml*	*2.0 ml*	*3.0 ml*
1. *p*-Hydroxybenzaldehyde	colorless	colorless	yellow tinge	yellow tinge	light orange brown	deeper orange brown
2. Sodium-4-hydroxybenzaldehyde-3-sulfonate	colorless	colorless	colorless	light yellowish pink	yellowish pink	deeper yellowish pink
3. 2-Hydroxy-5-chlorbenzaldehyde	strong yellow color	strong yellow color	deeper yellow color	deep yellow	deep yellow with slight greenish tinge	deeper yellow with slightly greener tinge
4. 2-Hydroxy-5-brombenzaldehyde	yellow	yellow	golden yellow	dark golden yellow	greenish yellow	greenish yellow
5. 2,4-Dithydroxybenzaldehyde	colorless	very light yellow	yellow with pinkish tinge	pink	reddish violet	reddish violet
6. 2-Hydroxy-3-methoxybenzaldehyde	yellowish orange	light orange	orange	reddish brown	reddish	reddish brown
7. 4-Hydroxy-3-methoxybenzaldehyde	light yellow	yellow	deep yellow	dark yellow with brown tinge	amber	dark amber
8. 2,3-Dimethoxybenzaldehyde	dark yellow	light orange	dark orange	strong reddish orange	reddish brown	dark reddish brown
9. 4-Hydroxy-3-methoxybenzaldehyde (vanillin)	light yellow	light greenish yellow	greenish yellow	strong greenish yellow	strong greenish brown	deep greenish brown
10. Hydroquinone-glucose (arbutin)	no reaction	no reaction [a]	yellow	yellow-brown	light brown	brown
	Concentration of compound					
	1.0% by weight			*5.0% by volume*		
	0.2 ml	*0.5 ml*	*1.0 ml*	*1.0 ml*	*2.0 ml*	*3.0 ml*
11. *o*-Hydroxybenzaldehyde	deep yellow	orange	reddish orange	cherry red	cherry red	cherry red
12. *o*-Methoxybenzaldehyde	reddish orange	dark cherry color	reddish purple	deep reddish purple	very deep reddish purple	very dark reddish purple
13. *p*-Methoxybenzaldehyde	light yellow	yellow	olive yellow	deep reddish purple	very deep reddish purple	very deep reddish purple
14. *o*-Ethoxybenzaldehyde	deep yellow	reddish brown	reddish purple	deep reddish purple	very deep reddish purple	very deep reddish purple
15. 3,4-Diethoxybenzaldehyde	red	cherry red	reddish violet	deep reddish violet	very deep reddish purple	very deep reddish purple

[a] Yellow on standing.

TABLE IV

REACTIONS OF PHENOLIC KETONES WITH SULFURIC ACID; DIFFUSION TESTS

Compound	*Concentration of compound*					
	0.1%			0.5%		
	0.2 ml	*0.5 ml*	*1.0 ml*	*1.0 ml*	*2.0 ml*	*3.0 ml*
1. *o*-Hydroxyacetophenone [a]	pale yellowish green	yellowish green	yellowish green	amber yellow	amber yellow	yellowish green
2. *p*-Hydroxyacetophenone	colorless	colorless	colorless	light yellow tinge	very light yellow	light golden yellow
3. *p*-Hydroxypropiophenone	colorless	colorless	colorless	greenish blue tinge	very light yellow	very light yellow
4. 4-(*o*-Hydroxyphenyl)-3-butene-2-one	deep yellow	orange	orange red	red	deep red	deep red
5. 2,4-Dihydroxyacetophenone (resacetophenone)	colorless	colorless	colorless	very light yellow	very light yellow	very light yellow
6. Anisalacetone	yellow tinge	light orange	orange	red	deep red	deep red
7. Vanillalacetone	deep yellow	orange	deep orange	deep red	reddish violet	deep reddish violet
8. 4-Hydroxybenzophenone	very pale green	light green	light green	yellow green	greenish yellow	lemon color
9. 4,4′-Dihydroxybenzophenone	very light yellow	light yellow with greenish tinge	yellowish green	lemon color	lemon color	lemon color
10. *p,p*′-Dimethoxybenzophenone [a]	pale yellow	light yellow	light yellow	yellow green in acid layer; green in benzene layer	yellow green in acid layer; green in benzene layer	yellow green in acid layer; green in benzene layer
11. Hydroxy-2-acetonaphthone	bright yellow	deep yellow	deep yellow	golden yellow	golden yellow	golden yellow
12. Quercetin	greenish	greenish	greenish	orange yellow	orange yellow	orange yellow
13. Rutin	light yellow	light yellow	light yellow	golden yellow	orange yellow	orange yellow

[a] This compound is a liquid. The concentrations represent per cent by volume for this compound, and for the others per cent by weight. The compounds, *o*-hydroxyacetophenone and *p,p*′-dimethoxybenzophenone, were made up in concentrations of 1.0% and 5.0%.

spectrum shows two peaks, one at 335 mμ and the other at 390 mμ. With the latter wave length a graph constructed with varying quantities of pyridoxal hydrochloride tested (10 to 100 μg) indicated that the color reactions followed the Beer-Lambert law. (Fig. 2). The color proved to be stable for at least 2 days when kept in the refrigerator at 40°F.

DISCUSSION

The vitamin B_6 group consists of pyridoxine, pyridoxal, and pyridoxamine. Pyridoxic acid constitutes a metabolic product eliminated by the kidneys. The first analytical procedures were developed when pyridoxine was believed to be the only compound that possessed the biologic characteristics of vitamin B_6. The colorimetric methods developed were based upon two chemical properties of pyridoxine. This compound possesses a phenolic hydroxyl and is a pyridine derivative.

The phenolic nature of pyridoxine gave rise to the development of colorimetric procedures typical of phenols. KERESZTESY AND STEVENS[7] and also GREEN[8] utilized ferric chloride as an analytical reagent with the resulting production of a red-brown color. KUHN AND LÖW[9] employed the phenol reagent of FOLIN AND DENIS[10] for the determination of pyridoxine. Several analytical procedures involve a coupling reaction with a diazo compound, a reaction characteristic of most phenolic compounds. SWAMINATHAN[11,12] employed diazotized sulfanilic acid and also diazotized *p*-nitroaniline, and BROWN, BINA AND THOMAS[13] employed diazotized *p*-aminoacetophenone. According to GIBBS[14], a phenol with an unsubstituted *para* position can form a blue indophenol compound. Pyridoxine is a phenol with an unsubstituted *para* position. STILLER, KERESZTESY AND STEVENS[15] showed that pyridoxine yielded a positive GIBBS reaction with 2,6-dichloroquinone chloroimide, and SCUDI and his collaborators[16–19] devised an analytical procedure based upon the finding of KERESZTESY AND STEVENS.

Two analytical procedures depend upon the fact that pyridoxine is a pyridine derivative. KUHN AND LÖW[9] developed the cyanine dye test, which is specific for α-picoline (2-methyl pyridine) and its derivatives. Pyridoxine is a 2-methyl pyridine derivative. The final product of the cyanine dye test is a violet complex, which shows absorption maxima at 599 mμ and at 555 mμ. SWEENEY AND HALL[20] developed the cyanogen bromide procedure. This procedure is based upon the fact that cyanogen bromide reacts with pyridine compounds to rupture the ring. The resulting compound is coupled with a diazotized aromatic amine. Although pyridoxine is a pyridine derivative, it does not react with cyanogen bromide because of the interference arising from the presence of the 2-methyl group. This methyl group is removed by oxidation to a carboxyl group, which on heating, is decomposed with the evolution of carbon dioxide. The demethylated pyridoxine reacts with cyanogen bromide, and the resulting compound is coupled with diazotized sulfanilic acid.

It is interesting to note whether various methods can be applied to differentiate the three vitamins (pyridoxine, pyridoxal and pyridoxamine) and the metabolite, pyridoxic acid. Pyridoxine forms a complex which does not react with 2,6-dichloroquinone chloroimide, while pyridoxal and pyridoxamine do react to form the blue dye. MELNICK *et al.*[21] observed that pyridoxal and pyridoxamine on an equimolar basis were about 15% and 31% as reactive as pyridoxine. ORMSBY, FISHER AND SCHLENK[22] observed that the three members of the vitamin B_6 group yielded different colors with diazotized sulfanilic acid. Pyridoxine gave an orange color, pyridoxamine an orange pink, and pyridoxal a bright yellow color. These colors were not very stable. With each compound the maximum intensity was reached one minute after the addition of the diazotized sulfanilic acid. The color developed with pyridoxine began to fade rapidly within 3 min, and the color developed with pyridoxal after about 5 min. Although the stability of the colors was limited in time, the investigators were able to obtain characteristic absorption spectra. According to METZLER AND SNELL[23] pyridoxal in alkaline solution exhibited a characteristic absorption band at about 390 mμ The color intensity varied with temperature and in the presence of pyridoxamine or amino acids. The reaction was not suitable for analytical purposes. Addition of an excess of ethanolamine, however, converted pyridoxal to a more highly colored complex, presumably a Schiff base, suitable for an analytical procedure.

Pyridoxic acid, according to SHIROISHI, FUKAI AND SAKURAI[24], yielded a dye with diazotized sulfanilic acid, but not with 2,6-dichloroquinone chloroimide. HUFF AND PERLZWEIG[25] developed for pyridoxic acid or its lactone a specific quantitative method based upon its characteristic fluorescent effects in the presence of hydrochloric acid. The sulfuric acid method is a quantitative procedure specific for pyridoxal.

SUMMARY

The carbonyl–phenol–acid reaction system yields color reactions with phenols, carbonyl compounds (aldehydes and ketones), and inorganic acids. To test for one of the components of this reaction system, the remaining two components constitute the specific reagents.

The four related compounds, pyridoxine, pyridoxamine, pyridoxal, and pyridoxic acid each possess a phenolic hydroxyl. Pyridoxal possesses an aldehyde group in addition to the phenolic hydroxyl. Pyridoxal yields an intense yellow color on treatment with concentrated sulfuric acid. Pyridoxine, pyridoxamine and pyridoxic acid prove not to be chromogenic on treatment with concentrated sulfuric acid. Pyridoxal can therefore be differentiated by means of the sulfuric acid reaction from the other three compounds related to vitamin B_6.

The colored product obtained by the interaction of pyridoxal and concentrated sulfuric acid yields a characteristic absorption spectrum and follows the Beer-Lambert law in the concentrations of pyridoxal tested (10–100 μg).

RÉSUMÉ

Le système carbonyl–phénol–acide permet d'obtenir des réactions colorées avec les phénols, les aldéhydes, les cétones et les acides inorganiques. On peut donc déterminer l'un des composés de ce système à l'aide des deux autres. Le pyridoxal, renfermant un groupe aldéhydique et un hydroxyle phénolique, donne avec l'acide sulfurique une coloration jaune; il peut ainsi être différentié de la pyridoxine, de la pyridoxamine et de l'acide pyridoxique. Le produit coloré obtenu par l'interaction du pyridoxal avec l'acide sulphurique concentré donne un spectre d'absorption caractéristique et suit la loi de Beer-Lambert dans les concentrations de pyridoxal étudiées, de 10–100 μg.

ZUSAMMENFASSUNG

Die Farbbildung des Systems: Carbonyl (Aldehyde und Ketone)–Phenole–Mineralsäuren kann zum Nachweis einer dieser Komponenten mit Hilfe der beiden anderen verwendet werden. Pyridoxal, das neben der phenolischen Hydroxylgruppe noch eine Aldehydgruppe besitzt, gibt mit Schwefelsäure eine intensive gelbe Farbe im Gegensatz zu Pyridoxin, Pyridoxamin und Pyridoxinsäure, die hierbei farblos bleiben. Das farbige Produkt der Reaktion von Pyridoxal mit konz. Schwefelsäure ergibt ein characteristisches Absorptions-spektrum und folgt dem Beer-Lambertschen Gesetz in den untersuchten Pyridoxal Konzentrationen von 10–100 μg.

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DETERMINATION OF POTASSIUM AND SODIUM IN MIXTURES OF THEIR SALTS BY MEANS OF CATION EXCHANGERS

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INTRODUCTION

This paper deals with some simple analytical applications of ion-exchange methods which, to judge from the available literature, have not previously been described. These methods are useful for the analysis of aqueous solutions (or water-soluble mixtures) of two substances if the qualitative composition of the solution or the mixture is known. The analyses described in this paper were performed with solutions of potassium chloride and sodium chloride. The methods are therefore illustrated by descriptions, of the determination of these two salts.

METHOD

In an aqueous solution containing potassium chloride and sodium chloride, the amounts of these salts (or of potassium and sodium) are to be determined. The analysis is performed in the following way:

A sample of the solution is evaporated, dried and accurately weighed. Another sample of equal volume is passed through a cation exchanger in the potassium or the sodium form. After washing with distilled water the combined effluent and wash-water are evaporated, dried and weighed. From these two weighings the content of potassium chloride and sodium chloride (and hence of potassium and sodium) are computed. The calculation is simple.

Suppose that, before the ion-exchange passage, the sample contains

$$a \text{ g KCl} + b \text{ g NaCl}$$

giving a total salt content of S_1 g. After the ion-exchange passage the following amounts are present in the combined effluent and wash-water, depending on whether the resin is in the potassium or the sodium form:

$$a \text{ g KCl} + \frac{M_{\text{KCl}}}{M_{\text{NaCl}}} \cdot b \text{ g KCl},$$

giving a total salt content of S_2 g, or

$$\frac{M_{\text{NaCl}}}{M_{\text{KCl}}} \cdot a \text{ g NaCl} + b \text{ g NaCl},$$

giving a total salt content of S_3 g.
From the above we find:

$$a + b = S_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$a + \frac{M_{\text{KCl}}}{M_{\text{NaCl}}} \cdot b = S_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\frac{M_{\text{NaCl}}}{M_{\text{KCl}}} \cdot a + b = S_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which M_{KCl} and M_{NaCl} denote the molecular weights of KCl and NaCl respectively. From eqn. (1) and eqn. (2) it follows that:

$$S_2 - S_1 = a + \frac{M_{\text{KCl}}}{M_{\text{NaCl}}} \cdot b - a - b = b \cdot \left(\frac{M_{\text{KCl}}}{M_{\text{NaCl}}} - 1\right) \quad . \quad . \quad . \quad (4)$$

and from eqn. (1) and eqn. (3):

$$S_1 - S_3 = a + b - \frac{M_{\text{NaCl}}}{M_{\text{KCl}}} \cdot a - b = a \cdot \left(1 - \frac{M_{\text{NaCl}}}{M_{\text{KCl}}}\right) \quad . \quad . \quad . \quad (5)$$

In these equations only a and b are unknown.

This method thus comprises the evaporation and drying of two samples of the solution to be analysed, one of the samples first being passed through a cation exchanger saturated with one of the ions present. Of course the salts must not be decomposed during the drying and should not be deliquescent. If necessary, the solution can be passed through an anion exchange resin, saturated with a suitable ion, in order to fulfil this condition.

The solution passed through the cation exchanger must not be acid, as in this case the hydrogen ions would, of course, also be exchanged. The solution must then be evaporated to drive off the acid, if volatile, or percolated through an anion exchanger in the hydroxyl form and then through another anion exchanger in, for instance, the chloride form.

The analysis may be performed in an alternative manner. The sample, containing potassium and sodium chloride, is dried and weighed as before. A sample of the same volume is passed through a strongly acid cation exchanger in the hydrogen form. The combined effluent and wash-water are titrated with standard alkali. The amounts of the salts in the solution are calculated as follows.

As before, suppose that the sample contains

$$a \text{ g KCl} + b \text{ g NaCl}$$

with a total salt content of S_1 g. Further let it be assumed that on titration after the ion-exchange passage c ml 1 N alkali hydroxide are consumed; then there are

$$\frac{1 \cdot c}{1000} = E \text{ equivalents}$$

in the sample. We then have:

$$a + b = S_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{a}{M_{\text{KCl}}} + \frac{b}{M_{\text{NaCl}}} = E \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where M_{KCl} and M_{NaCl} as before denote the molecular weights of potassium chloride and sodium chloride respectively. From eqn. (1) and eqn. (6) it follows that:

$$\frac{S_1 - b}{M_{\text{KCl}}} + \frac{b}{M_{\text{NaCl}}} = E \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$S_1 \cdot M_{\text{NaCl}} - b \cdot M_{\text{NaCl}} + b \cdot M_{\text{KCl}} = E \cdot M_{\text{KCl}} \cdot M_{\text{NaCl}}$$

$$b = \frac{E \cdot M_{\text{KCl}} \cdot M_{\text{NaCl}} - S_1 \cdot M_{\text{NaCl}}}{M_{\text{KCl}} - M_{\text{NaCl}}} = \frac{M_{\text{NaCl}}}{M_{\text{KCl}} - M_{\text{NaCl}}} \cdot (E \cdot M_{\text{KCl}} - S_1)$$

$$a = \frac{M_{\text{KCl}}}{M_{\text{KCl}} - M_{\text{NaCl}}} \cdot (S_1 - E \cdot M_{\text{NaCl}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This method thus comprises the evaporation and drying of a sample of the solution to be analysed, and titrating another sample of the same volume with standard alkali, after it has passed a cation exchanger in the hydrogen form.

Estimation of the error

With the first method decsribed above, the ion that is present in excess may conveniently be exchanged in order to get optimum accuracy in the analysis; this is shown by the following example.

The mixture to be analysed contains 90 mole% potassium chloride and 10 mole% sodium chloride. If the sample taken contains 9 mequiv. of KCl and 1 mequiv. of NaCl we have:

Before the ion exchange: 0.67095 g KCl + 0.05845 g NaCl = 0.7294 g total salt = S_1. After exchange against potassium ions: 10 mequiv. of KCl = 0.7455 g = S_2.

$$S_2 - S_1 = 0.7455 - 0.7294 = 0.0161 \text{ g}$$

After exchange against sodium ions: 10 mequiv. of NaCl = 0.5845 g = S_3.

$$S_1 - S_3 = 0.7294 - 0.5845 = 0.1449 \text{ g}$$

Suppose that the error in the weighings is 1.0 mg. The maximum error in both cases is therefore 2.0 mg. The % error in the first case is 200/16.1 = 12.4%, whereas in the second case the maximum relative error is 200/144.9 = 1.4%.

If we suppose that the solution contains the same amount of potassium chloride and sodium chloride then a sample of 1 g salt contains:

$$0.5 \text{ g KCl} + 0.5 \text{ g NaCl} = 1.0 \text{ g} = S_1$$

After exchange against potassium ions:

$$0.5 + \frac{M_{\text{KCl}}}{M_{\text{NaCl}}} \cdot 0.5 = 1.1377 \text{ g} = S_2$$

$$S_2 - S_1 = 1.1377 - 1.0 = 0.1377 \text{ g}$$

The maximum relative error is $\frac{200}{137.7} = 1.46\%$

After exchange against sodium ions:

$$\frac{M_{\text{NaCl}}}{M_{\text{KCl}}} \cdot 0.5 + 0.5 = 0.8920 \text{ g} = S_3$$

$$S_1 - S_3 = 1.0000 - 0.8920 = 0.1080 \text{ g}$$

The maximum relative error is $\frac{200}{108.0} = 1.86\%$

From these simple calculations it can be seen that, if the total salt content in the sample is about 1 g and the error in the weighings 1.0 mg, the maximum relative error is $< 2\%$, when the analysis is performed in the most suitable way.

In a similar manner the maximum relative error in the second way of performancing the analysis may be estimated. In this case, however, the differences $(S_1 - E \cdot M_{\text{NaCl}})$ or $(E \cdot M_{\text{KCl}} - S_1)$ respectively, occur in the formula and these are generally small. Even small errors in the weighings therefore give relatively large errors in the calculations. The maximum relative error in this case is therefore larger but ought in every case to be $< 6\%$.

EXPERIMENTAL

Apparatus

The cation exchanger used was Amberlite IR-120 (Rohm & Haas Co., Philadelphia, U.S.A.), which is of sulfonic acid type. The particle size was 0.15–0.30 mm in air dry condition. Ion-exchange columns of ordinary type were used, the diameter and height of the resin layer being 10 mm and 160 mm respectively.

The resin was transformed into the desired form by passing 100 ml of 3–4N solution of the corresponding chloride through the column, followed by subsequent washing with distilled water, until no traces of chloride could be detected in the filtrate. In order to transform the resin to the hydrogen form 100 ml 2N HCl was passed through the ion-exchange layer, afterwards washing the resin with distilled water until neutral reaction of the effluent. The flow-rate during regeneration and washing was about 5 ml/min.

Procedure

Solutions containing varying amounts of potassium and sodium chloride were used in the experiments. The solutions were prepared from salts of analytical reagent grade, which were dried at about 150° and accurately weighed. Samples of 10 ml were percolated through the ion-exchange layer; after washing with 50 ml distilled water the combined effluent and wash-water were dried and the residue accurately weighed; when the resin was in the hydrogen form the combined effluent and wash-water were titrated with 1N NaOH. 10 ml of the original solution were also evaporated and dried and the salt residue accurately weighed. The potassium and sodium chloride in the solutions were then calculated as described above. The results are presented in Tables I and II.

TABLE I

Added, g/l		*Found, g/l*							
		After passage through K-saturated resin				*After passage through Na-saturated resin*			
NaCl	*KCl*	*NaCl*	*% relative error*	*KCl*	*% relative error*	*NaCl*	*% relative error*	*KCl*	*% relative error*
0.2502	0.7505	0.2360	—5.68	0.7638	+1.77	0.2523	+0.84	0.7475	—1.03
0.3641	0.6366	0.3768	+3.46	0.6260	—1.66	0.3721	+0.25	0.6480	+1.76
0.4577	0.5430	0.4533	—0.92	0.5402	—0.52	0.4601	+0.52	0.5397	—0.61
0.5003	0.5004	0.5022	+0.34	0.4944	—1.20	0.5060	+1.10	0.4916	—1.76
0.6862	0.3145	0.6832	—0.44	0.3180	+1.11	0.6913	+0.74	0.3083	—1.97
0.7508	0.2499	0.7523	+0.20	0.2558	+1.44	0.7354	—2.04	0.2657	+6.32
0.8419	0.1588	0.8410	—0.16	0.1580	—0.51	0.8023	—4.70	0.1703	+7.02

TABLE II

Added, g/l		*Equivalents added*	*Equivalents found after passage through H-saturated ion exchanger*	*Found, g/l*			
NaCl	*KCl*			*NaCl*	*% relative error*	*KCl*	*% relative error*
0.2502	0.7505	0.01435	0.01440	0.2643	+5.65	0.7362	—1.90
0.4577	0.5430	0.01511	0.01515	0.4672	+2.08	0.5334	—1.77
0.6862	0.3145	0.01596	0.01591	0.6730	—1.92	0.3278	+4.23
0.8419	0.1588	0.01653	0.01656	0.8491	+0.86	0.1519	—4.35

As can be seen from Table I the errors in this type of analysis, which involves two weighings, are larger the smaller the weight-differences before and after ion-exchange passage. This is in accordance with the estimation of the error given above. It is, however, always possible to perform the analysis in such a manner that the error in the determination is less than 2%. In most cases it is, of course, impossible to know which constituent is present in larger amount, and it is therefore advisable to percolate the solution through both the sodium and the potassium form of the cation exchanger. The analysis then comprises 3 weighings, with a maximum relative error of 2%.

Table II shows that the maximum relative error in this case is larger, which agrees with the above estimation. This analysis is, however, simpler, since it involves only one weighing and one standard titration.

DISCUSSION

Of the methods described in this paper the first one, comprising only weighings, is obviously very suitable for the analysis of a mixture of two difficultly separable salts. Besides solutions of potassium and sodium salts, solutions of two alkaline earth metal salts or of nickel and cobalt salts may be mentioned. Of course the method may also be applied to the determination of negative ions, if the cation exchanger is replaced by an anion exchanger. The points discussed are likewise valid in this case.

As has been stated above the second method, comprising weighing and titration, is not so accurate as the first one. The method is, however, simple, but it is probably not sufficiently accurate for most analyses.

SUMMARY

Methods for the determination of two substances in aqueous solutions (or water-soluble mixtures) are described. A sample of the solution is dried and the residue accurately weighed. Another sample of the same volume is passed through a cation exchanger (when cations are to be determined), saturated with one of the ions in the solution. After washing with distilled water the combined effluent and wash-water are dried and the residue carefully weighed. From these weighings the composition of the solution is determined by simple calculations, the maximum relative error being $< 2.0\%$. The method may be used for the determination of anions, if an anion exchanger is used instead of the cation exchanger.

A variation of the method consists in passing the solution through a cation exchanger in the hydrogen form. The number of equivalents is determined by standard alkali titration and from this and the weight before the ion-exchange passage the composition of the solution can be determined. In this case, however, the maximum relative error is larger. This method is directly applicable to the determination of anions.

RÉSUMÉ

Des méthodes sont décrites pour le dosage de deux substances en solution aqueuse. On procède d'abord par évaporation d'un volume determiné de l'échantillon à analyser et pesée du résidus. On traite ensuite un volume égal de cette solution à analyser par un échangeur d'ions approprié. On évapore l'éluat et on pèse; par un simple calcul, on peut alors déterminer la composition recherchée. On peut également utiliser un échangeur de cations (forme hydrogène) et titrer par une solution étalon d'hydroxyde alcalin.

ZUSAMMENFASSUNG

Es werden Methoden zur Bestimmung von zwei verschiedenen Substanzen (z.B. Kationen) in wässriger Lösung beschrieben. Ein bestimmtes Volumen der Lösung wird zur Trockne gedampft und der Rückstand gewogen. Ein gleiches Volumen der Lösung wird mit einem Kationenaustauscher Harz, das mit einem der Kationen beladen ist, behandelt und das Eluat ebenfalls zur Trockne gedampft und der Rückstand gewogen. Aus der Gewichtsdifferenz lässt sich dann die Zusammensetzung der ursprünglichen Lösung berechnen. Man kann die Lösung auch mit einem Kationenaustauscher in der H-Form behandeln und das Eluat mit einer Standard-Alkalilauge titrieren.

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SUR LA THERMOGRAVIMÉTRIE DES PRÉCIPITÉS ANALYTIQUES
LXV. DOSAGE DE L'IRIDIUM*

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et

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Nous avons relevé[1] dans un article récent, les modes de dosage gravimétrique proposés jusqu'ici pour l'iridium. On peut faire la pesée sous forme de métal en précipitant soit par l'acide formique, soit par le mercapto-2 benzothiazole, ou encore à l'état de sulfure.

1. *En metal par l'acide formique*

La précipitation se fait, comme d'habitude, en présence du tampon d'acétate d'ammonium. Toute la difficulté se présente lorsqu'il s'agit de rassembler le précipité qui prend facilement une nature colloïdale. C'est pourquoi, nous avons utilisé le mode opératoire suivant que nous croyons recommandable.

Nous prenons un des creusets filtrants de verre déjà décrits[2] et garnissons le fond de soie de quartz qui retient bien l'iridium colloïdal en son centre. Après lavage soigné, la petite pastille est décollée avec soin puis transférée dans l'un des creusets adaptables sur l'anneau de la thermobalance. On pourrait aussi prendre, naturellement, un petit vase de silice percé à sa base de trous et garni de soie de silice. En effet, après chauffage, pesée, on a toute latitude pour attaquer cette soie par l'acide fluorhydrique et récupérer ainsi l'iridium; autrement il n'est guère possible de nettoyer un creuset de verre ou de silice frittés. Il n'est pas question non plus d'effectuer la filtration sur papier.

Ceci posé, l'iridium ainsi précipité nous a donné par inscription sur la thermobalance, une droite parfaitement horizontale jusqu'à 879°. Nous croyons donc parfaitement inutile de compliquer ce dosage en effectuant le chauffage, puis le refroidissement dans l'hydrogène, puis dans l'azote, comme on le fait encore à l'heure actuelle. Cette droite horizontale ne sera pas reproduite.

2. *Avec le mercapto-2 benzothiazole*

Le précipité volumineux, orangé, préparé comme l'indiquent BAREFOOT, McDONNELL ET BEAMISH[3], ne présente pas de palier de poids constant quoique la courbe s'infléchisse assez nettement entre 135 et 250°. Cela correspond sensiblement à un atome d'iridium pour 3.8 molécules de mercaptobenzothiazole (poids moléculaire calculé: 837) (Fig. 1). La matière organique se détruit ensuite et à 520°, on obtient le poids constant en iridium métal, qui se maintient au moins jusqu'à 980°.

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* Pour LXIV (Rhodium), voir[5].

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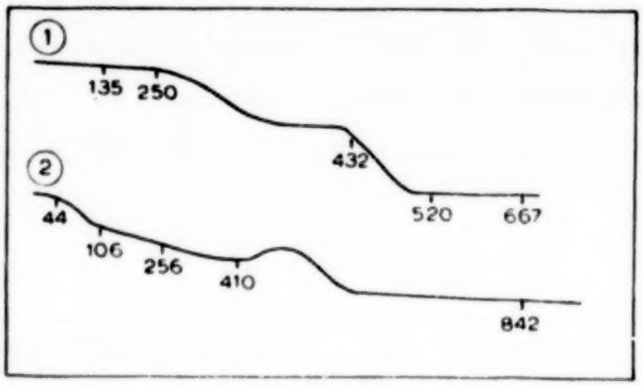

Figs. 1 et 2

3. *Précipitation en sulfure*

En utilisant le sulfure de sodium, TAIMNI ET SALARIA[4] obtiennent un précipité qu'ils séchent à 85° et auquel ils attribuent la formule $Ir_2S_3 \cdot 10H_2O$. Nous avons reproduit cette expérience, ce qui nous a donné la courbe de thermolyse (Fig. 2) montrant nettement que ce précipité ne présente pas de palier dans la région de 85° où la courbe descend d'une manière abrupte. La perte de poids a lieu dès la température ordinaire et au-dessus de 410°, il se produit une légère réoxydation qui pourrait être attribuée à un passage de sulfure en sulfate. Après quoi, il y a de nouveau perte de poids pour arriver vers 800° à l'iridium métal. On n'e peut donc pas faire entrer cette méthode en ligne de compte.

RÉSUMÉ

Nous avons enregistré la courbe de thermolyse des précipités contenant de l'iridium et obtenus respectivement avec l'acide formique, le mercapto-2 benzothiazole et le sulfure de sodium.

SUMMARY

Thermolysis curves have been recorded of precipitates containing iridium, obtained with formic acid, 2-mercapto-benzothiazole and sodium sulphide respectively.

ZUSAMMENFASSUNG

Es wird der Verlauf (Kurven) der Thermolyse von Iridium-haltigen Niederschlägen, die mit Ameisensäure, Mercapto-2-benzothiazol oder Natriumsulfid erhalten wurden, beschrieben.

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SUR LA THERMOGRAVIMÉTRIE DES PRÉCIPITÉS ANALYTIQUES
LXVI. DOSAGE DU HAFNIUM*

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OBTENTION DE LA MATIÈRE PREMIÈRE

L'oxychlorure de hafnium $HfOCl_2 \cdot 8H_2O$ nécessaire pour effectuer ce travail, a été obtenu par la méthode STREET ET SEABORG[1] en faisant usage de la résine Dowex-50, passée sur tamis à 100 trous. On ajoute peu à peu 150 mg d'oxychlorure de zirconium du commerce, produit Merck, à une suspension de 2 ml de Dowex dans 45 ml d'acide perchlorique 2*N* et, au bout d'un quart d'heure, le petit paquet de résine obtenu est disposé au sommet d'une colonne neuve, préalablement permutée en ions H^+ par une liqueur d'acide chlorhydrique *N*. On élue ensuite par l'acide chlorhydrique 6*N*. On sait que l'on obtient dans les 60 premiers ml isolés, 66% de l'oxyde de hafnium primitif ne contenant plus que 1% d'oxyde de zirconium.

La pureté définitive du produit a été contrôlée spectrographiquement et comparée à celle d'un échantillon d'oxychlorure de hafnium pur mis gracieusement à notre disposition par Monsieur le Professeur C. J. VAN NIEUWENBURG (Delft), que nous sommes heureux de remercier ici.

Dans le LIe mémoire de cette série[2], on trouve une étude sur les courbes de thermolyse effectuées avec de l'oxychlorure de zirconium brut et de l'oxychlorure de zirconium exempt de hafnium. Nous n'avons pas reproduit toutes ces courbes dans le cas du hafnium pur ; nous nous sommes limités à l'étude de 6 précipités que nous croyons caractéristiques et utiles pour le dosage du hafnium, c'est-à-dire la formation d'hydroxyde (par l'ammoniaque, par l'ammoniac, par le tannin), de sélénite (basique et neutre), de mandélate, de *p*-hydroxyphénylarsinate, de phosphate et de cupferronate.

Chaque fois nous avons comparé la courbe de thermolyse due au hafnium et celle due au zirconium, les précipitations étant faites dans les mêmes conditions.

A. Par l'ammoniaque

On observe d'abord (Fig. 1) une rapide perte d'eau jusqu'à 199° dans le cas d'un chauffage linéairement croissant, à raison de 300°/h et pour un poids d'oxyde de hafnium résiduel correspondant à 45.9 mg. Ensuite, la perte de poids est plus lente et l'eau de constitution s'échappe à partir de 270° environ. On n'observe aucun accident sensible correspondant aux compositions $HfO(OH)_2$ et $Hf(OH)_4$; on obtient le palier de l'oxyde HfO_2 à partir de 350° (dans les mêmes conditions il faut chauffer jusqu'à 400° pour obtenir l'oxyde de zirconium anhydre). Ainsi donc, cette méthode permet d'opérer à température relativement basse, mais le manque de sélectivité est le gros inconvénient.

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* Pour LXV (Iridium) voir[14].

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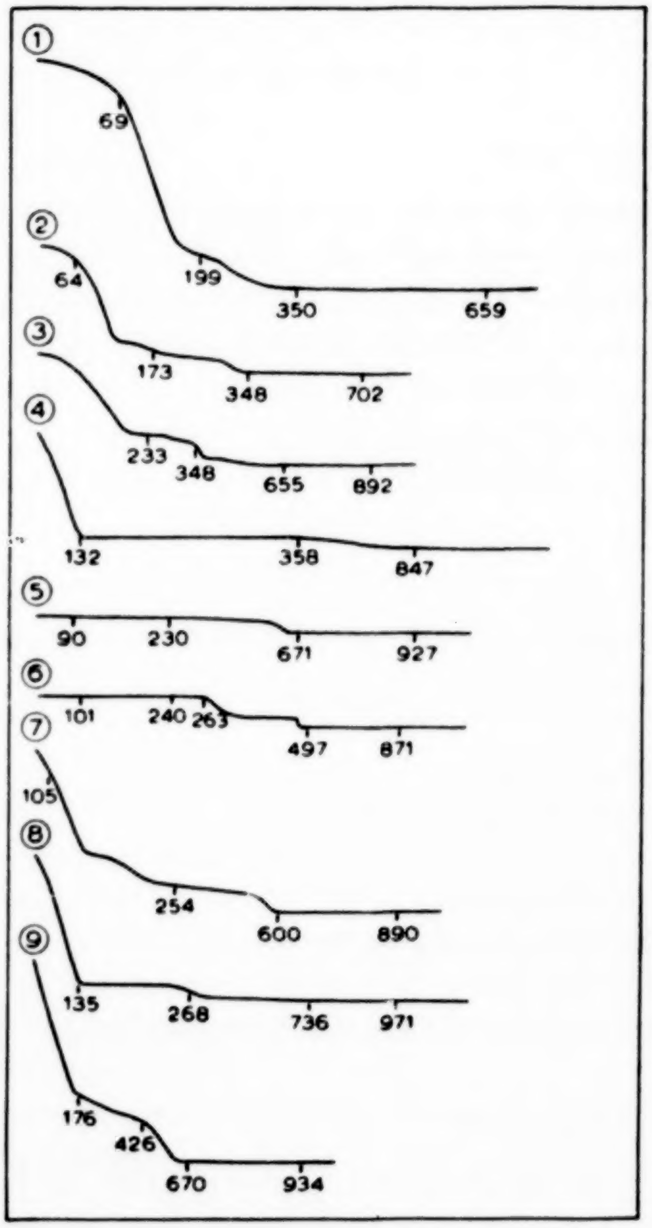
B. Par l'ammoniac

La précipitation est effectuée avec un lent courant d'air chargé de gaz ammoniac suivant la méthode de TROMBE[3] que nous avons utilisée bien des fois au cours de cette étude. La courbe de thermolyse obtenue (Fig. 2) ressemble beaucoup à la précédente. La déshydratation se poursuit lentement jusqu'à 350° où l'on atteint le palier de l'oxyde tout au moins avec les poids indiqués ci-dessous. Un dosage de hafnium exécuté par cette méthode fournit 5.3 ± 0.5 mg d'après la mesure sur le papier graphique, pour une quantité d'oxyde de hafnium de 5.272 ± 0.001 mg mesurée sur la microbalance.



Figs. 1–9.

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C. Par le tannin

Nous avons utilisé la méthode de SCHOELLER[4]. La courbe obtenue (Fig. 3) est tout à fait identique à celle du zirconium. On obtient l'oxyde de hafnium à partir de 655° et celui de zirconium à partir de 880°. Nous n'avons pas observé la légère remontée de la courbe signalée dans le cas du zirconium et attribuée à une réduction, puis à une réoxydation de la zircone.

D. Précipitation en sélénite basique

Nous avons utilisé la méthode proposée par CLAASSEN pour le zirconium[5]. Le palier observé sur la Fig. 4 ne correspond à aucun composé défini, comme le montre le calcul et comme nous l'avions déjà constaté d'ailleurs pour le précipité homologue de zirconium.

E. Précipitation en sélénite neutre

Mais par la technique de CLAASSEN, si on laisse digérer le précipité de sélénite de hafnium pendant plusieurs heures à 80°, on obtient un précipité cristallin correspondant bien à la composition $Hf(SeO_3)_2$. La courbe de thermolyse de ce précipité est représentée sur la Fig. 5. Le sélénite de hafnium se décompose à température nettement inférieure à celle du sélénite de zirconium:

$Hf(SeO_3)_2$ à partir de 230°

$Zr(SeO_3)_2$ à partir de 537°

La méthode peut servir pour le dosage du hafnium et de deux manières: soit en pesant le sélénite, soit en pesant l'oxyde:

Poids d'oxyde de hafnium pesé	10.060 ± 0.001 mg
Poids d'oxyde de hafnium mesuré sur la courbe	10.8 ± 0.5 mg
Poids de sélénite de hafnium pesé	22.750 ± 0.001 mg
Poids de sélénite de hafnium mesuré sur la courbe	23.8 ± 1 mg

Le facteur analytique est très favorable: $HfO_2/Hf(SeO_3)_2 = 0.4869$.

F. Précipitation en mandélate

En généralisant la méthode de KUMINS[6] et de HAHN ET BAGINSKY[7], nous avons obtenu le précipité de tétramandélate de hafnium dont la composition correspond à la formule $Hf(C_6H_5CHOHCO_2)_4$; celui-ci est stable jusqu'à 240° comme le prouve la courbe de thermolyse de la Fig. 6. Il commence alors à se décomposer très lentement, puis plus rapidement à partir de 263° et à 497° commence le palier horizontal de l'oxyde. Comme dans le cas du zirconium, il y a sans doute une légère réduction de cet oxyde à cause de l'atmosphère réductrice qui règne dans le four.

Ce réactif est très spécifique et possède aussi un facteur analytique avantageux: $HfO_2/Hf(C_8H_7O_3)_4 = 0.2689$.

G. Précipitation en p-hydroxyphénylarsinate

Nous avons suivi les indications de CLAASSEN[8], ce qui donne un précipité blanc, floconneux et très sélectif. Les courbes de thermolyse des *p*-hydroxyphénylarsinates de hafnium et de zirconium (Fig. 7) sont tout à fait semblables; il ne semble pas y avoir de composé défini; pour le hafnium la courbe est constamment décroissante jusqu'à 600°; on obtient le palier de l'oxyde à partir de 770°.

Là encore, depuis 600°, on constate une augmentation de poids du corps chauffé; on l'attribue à une réoxydation du hafnium, consécutive à la réduction exercée dans le four par l'anhydride arsénieux et l'oxyde de carbone. Il s'agit d'une excellente méthode de dosage. En effet, l'un de nos essais nous donne:

Poids d'oxyde de hafnium pesé	11.85 ± 0.01 mg
Poids d'oxyde de hafnium mesuré sur la courbe	11.9 ± 0.6 mg

H. Précipitation en phosphate

En suivant la méthode proposée pour le zirconium par STUMPFER ET METTELOCK[9] utilisant le phosphate diammonique, nous avons obtenu un précipité riche en eau dont il perd une grande partie jusqu'à 135° (Fig. 8). Le palier intermédiaire ne s'adapte avec aucune formule simple. A partir de 350°, on obtient un phosphate correspondant à la formule $(HfO)HPO_4$ qui se déshydrate lentement puis, on aboutit au composé HfP_2O_7 ou pyrophosphate vers 700°. Les résultats sont tout à fait d'accord avec ceux obtenus pour le zirconium. La précision est bonne puisque un dosage nous donne:

HfP_2O_7 calculé	5.221	mg
HfP_2O_7 mesuré	5.30	mg

mais il est difficile de récupérer ensuite le hafnium combiné au phosphore.

I. Précipitation en cupferronate

La précipitation effectuée avec le cupferron suivant la méthode de SCHRÖDER[10], FERRARI[11] conduit à un précipité très instable, aussi bien pour le hafnium que pour le zirconium, qui perd du poids constamment jusqu'à 745° pour le zirconium et 670° pour le hafnium (Fig. 9). Ce précipité n'est pas spécifique; il faut peser en oxyde. Cependant, on peut y avoir recours si l'on effectue la précipitation en milieu très acide ou si l'on fait un entraînement.

Tableau I donne les réactifs étudiés pour le dosage gravimétrique du hafnium, les formes de pesée et les limites de température.

PREMIÈRE NOTE

Sur la récupération du hafnium

Nous voulons indiquer, à toutes fins utiles, comment se fait la préparation de l'oxychlorure de hafnium à partir des résidus du chauffage dans la thermobalance.

a) Au départ de l'oxyde de hafnium. On l'attaque par fusion avec le pyrosulfate de sodium ou par l'acide sulfurique concentré, au bain de sable. On reprend le résidu par l'acide sulfurique au demi et chaud, filtre, précipité l'hydroxyde par l'ammoniaque,

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TABLEAU I

Réactif	*Forme de pesée*	*Limites de températures*
Ammoniaque	HfO_2	>350°
Ammoniac	HfO_2	>500°
Tannin	HfO_2	>655°
* Acide sélénieux	$Hf(SeO_3)_2$	90–220°
	HfO_2	>680°
* Acide mandélique	$Hf\ (C_6H_5\text{-}CHOH\text{-}CO_2)_4$	90–260°
	HfO_2	>500°
Acide *p*-hydroxyphénylarsinique	HfO_2	>660°
Phosphate diammonique	HfP_2O_7	>750°
Cupferron	HfO_2	>670°

* Nous avons indiqué par un astérisque celles des méthodes que nous proposons pour la gravimétrie automatique.

filtre de nouveau, lave le précipité avec de l'eau ammoniacale jusqu'à disparition des ions SO_4^{-2} dans la liqueur filtrée ; on dissout alors l'hydroxyde dans l'acide chlorhydrique, évapore au bain-marie. Parfois, le corps cristallisé possède une coloration jaune pâle due à la fois à des traces de fer et à du tétrachlorure de hafnium. On peut, naturellement, séparer des traces de fer en appliquant la méthode d'extraction mise au point par SWIFT[12] et DODSON, FORNEY ET SWIFT[13]; on dissout l'oxychlorure brut dans 20 ml d'acide chlorhydrique 8*N* puis, on fait l'extraction par 50 ml d'éther isopropylique et on fait cristalliser la phase aqueuse sous vide.

b) Au départ du pyrophosphate. On fait une fusion de ce dernier en creuset de platine, avec le carbonate neutre de sodium. On reprend par l'acide chlorhydrique et précipite le hafnium par le cupferron, seul réactif usuel permettant une précipitation en présence de phosphate ; on chauffe à 900° pour obtenir l'oxyde, que l'on met en solution comme ci-dessus.

DEUXIÈME NOTE

Essai par spectrographie infrarouge

Nous avons tenté d'obtenir à l'état solide, les spectres d'absorption infrarouge des oxychlorures de hafnium et de zirconium, en vue de trouver les fréquences propres des groupes prétendus HfO et ZrO. L'expérience a été négative ; avec différentes épaisseurs de cuve, nous n'avons pu observer de bandes entre 6 et 38 μ. On peut donc conclure que ou bien les fréquences caractéristiques sont à rechercher au-dessus de 38 μ, ou bien que ces deux groupements n'existent pas.

RÉSUMÉ

Les auteurs ont préparé de l'oxychlorure de hafnium exempt de zirconium et tracé les courbes de thermolyse des précipités permettant de doser gravimétriquement le hafnium. Leur attention se porte surtout sur le séléniate neutre, le *p*-hydroxyphénylarsinate et le mandélate. Les courbes obtenues ont été comparées à celles que l'on peut former avec les dérivés homologues du zirconium.

SUMMARY

A zirconium-free oxychloride of hafnium was prepared. The hafnium can be determined gravimetrically from the thermolysis curves of the precipitate. In particular, the neutral selenate, the *p*-hydroxyphenylarsinate and the mandelate were studied, and the curves obtained were compared to those plotted of the homologous zirconium derivatives.

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ZUSAMMENFASSUNG

Es wird die Herstellung eines zirkoniumfreien Hafniumoxychlorides beschrieben. Aus dem Verlauf der Thermolyse (Kurven) der Niederschläge lässt sich das Hafnium gravimetrisch bestimmen. Hervorgehoben werden das neutrale Selenat, das *p*-Hydroxyphenylarsenat und das Mandelat. Die erhaltenen Kurven werden mit denjenigen der entsprechenden Zirkoniumverbindungen verglichen.

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THE DETERMINATION OF THE SOLUBILITY OF ORGANIC SOLVENTS IN MINERAL ACIDS

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INTRODUCTION

Thermodynamic or mass-action treatments of the partition of mineral acids between aqueous solutions and organic solvents[1-3] tacitly assume that the equilibrium can be represented by an equation such as

$$R_2O_{(org)} + HX_{(aq)} \rightleftarrows R_2O \cdot HX_{(org)}$$

where the subscripts indicate the phase in which the species exist. It is important in this respect to be certain that the aqueous phase contains no significant amount of either the solvent or the acid-base complex, both of which are assumed to be completely insoluble in the mineral acid. This point has been discussed by Sutton[4] with reference to the system H_2O/HNO_3/di-ethyl ether, where the solvent is appreciably soluble in the aqueous phase. This type of solubility is of further interest in relation to the solvation of mineral acids in aqueous solution[5,6].

The methods available for the determination of such solubilities have been discussed by Campbell, Laurene and Clark[6]. These authors examined changes of surface tension, refractive index, viscosity and density and found that only the density variation was suitable for use in comparative measurements of the ether concentration in aqueous hydrochloric acid. The method described below depends on the direct determination of the amount of solvent thrown out of an aliquot of the aqueous phase on neutralization; it has been tested by a series of experiments on the iso-propyl ether/HCl system, for which results are already available from the work of CAMPBELL *et al.*

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EXPERIMENTAL

Materials

Pure iso-propyl ether was shaken with aqueous sodium carbonate, washed several times with water, dried over anhydrous magnesium sulphate, and treated with chromatographic alumina to remove peroxides[7].

Analytical grade hydrochloric acid was suitably diluted some time before use; acid concentrations were determined by titration with standard alkali.

Centrifuge tubes

The centrifuge tube used in this work is that designed for the Babcock test (fat content of human milk), and shown in Fig. 1. The total volume to the bottom of the narrow neck is approximately 7.5 ml; the neck is ∿ 4.5 cm long. The tubes were calibrated by measuring the increase in weight due to the addition of a small amount of water to a tube already almost completely filled. The increase in the height of the liquid in the neck was measured with a travelling microscope.

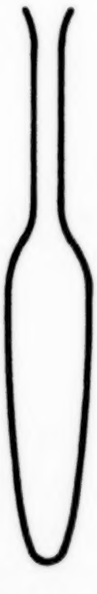

Fig. 1. Centrifuge tube for Babcock test.

Procedure

As an illustration of the experimental technique, measurements on the H_2O/HCl/iso-propyl ether system will be described. All experiments were carried out at room temperature, which remained constant throughout at 23°.

Equal volumes of aqueous hydrochloric acid and iso-propyl ether were shaken together for 30 min in a stoppered bottle. The (upper) organic phase was then completely removed and an aliquot of the aqueous phase titrated to determine the acid concentration. A suitable aliquot (generally 1–3 ml) of the aqueous solution was placed in the centrifuge tube and neutralized with strong (25% w/w) caustic soda solution. The use of an indicator during neutralization is not recommended, since this tends to precipitate and subsequently collect at the liquid–liquid interface, making the meniscus obscure and difficult to measure. Cooling of the centrifuge tube was required to dissipate the heat of neutralization and to prevent evaporation of the ether. Mechanical stirring of the liquid was not found to be necessary.

Sufficient caustic soda and/or water were added to bring the ether into the calibrated neck of the tube which was then centrifuged for a few minutes. The tube was left to reach room temperature, after which the height of the column of ether was measured with a travelling microscope. It was found advisable to cork the neck of the tube before centrifuging; this prevents both evaporation of the ether and accumulation of dust at the liquid–liquid interface.

RESULTS AND DISCUSSION

Reproducibility and calibration

The accuracy of the method was initially tested simply by measuring the height of the column of iso-propyl ether obtained from equal aliquots of the same solution.

Two such series gave

$$1.37,\ 1.36,\ 1.35\ \text{cm}$$
$$\text{and } 0.43_0,\ 0.42_5,\ 0.41_5\ \text{cm}$$

showing that the results are reproducible to within 1% for identical conditions. It soon became clear however, that the results obtained from different aliquots varied systematically with the volume of solution taken. The results of three such experiments are shown in Fig. 2.

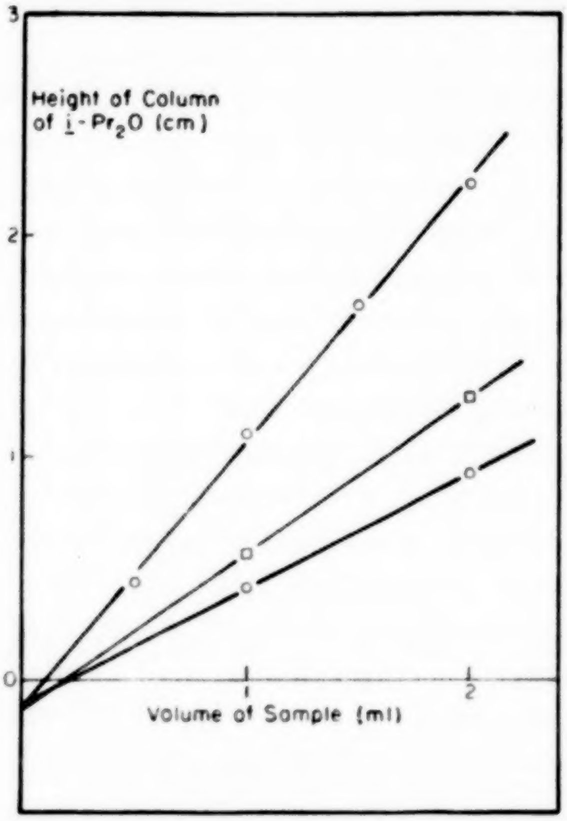

Fig. 2. Variation of height of column of iso-propyl ether with volume of sample.

The intercept from these three experiments is reasonably constant at 0.13 ± 0.01 cm, and corresponds to a solubility of 0.15 g iso-propyl ether per 100 ml of the final aqueous solution of caustic soda and sodium chloride. In making a correction for this effect it is assumed that the volume and composition of the final neutralized solution in the centrifuge tube are constant. This is not strictly true, but the errors introduced by the small variations in these factors are certainly negligible for any but the most refined measurements. The zero correction needs to be determined separately, of course, for each organic solvent.

Calibration of five tubes by the method already described gave the capacity of the cylindrical neck as

0.120, 0.119, 0.117, 0.120, 0.119 ml/cm

yielding as the mean value for any individual tube 0.119 ± 0.002 ml/cm. From this one can calculate the calibration factor for iso-propyl ether (density 0.726 g/ml, molecular weight 102) as

$$[\text{i-Pr}_2\text{O}] = \left(\frac{h + 0.13}{V}\right) \cdot \frac{0.119 \times 0.736 \times 10^3}{102}$$

where [i-Pr_2O] is the molar concentration of iso-propyl ether in the solution under examination, h the height of the ether column in the tube (in cm) and V the volume of sample taken (in ml). This equation reduces to

$$[\text{i-Pr}_2\text{O}] = \left(\frac{h + 0.13}{V}\right) \times 0.847$$

Any errors arising from differences in the shape of the ether-air and ether-aqueous solution menisci are certainly negligible.

Solubility of iso-propyl ether in aqueous hydrochloric acid

The results of a series of determinations of the solubility of iso-propyl ether in aqueous hydrochloric acid are shown in Fig. 3. This diagram also shows the results reported by CAMPBELL, LAURENE AND CLARK[6] for this system at 20°, based on measurements of the density of the solution.

Two main points emerge immediately from Fig. 3. One is the sharp rise in the solubility at about $7M$ hydrochloric acid; this effect has been discussed in terms of the solvation of the proton[6]. Similar (but larger) changes have been noted by LEJEUNE[5] for the solubility of di-ethyl ether in perchloric acid. The other interesting feature is the marked temperature coefficient of the solubility in this region; the behaviour of the di-ethyl ether–perchloric acid system is very similar[8]. It is also worth noting that the present method apparently gives results whose reproducibility is as good as, or better than, those found from the density measurements.

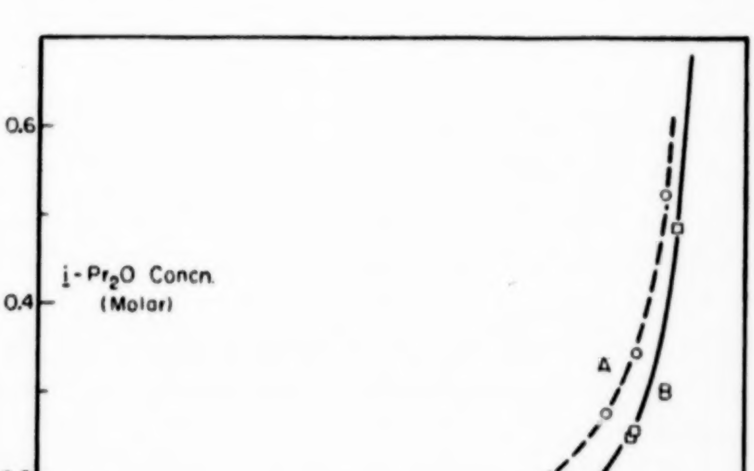

Fig. 3. Solubility of iso-propyl ether in aqueous hydrochloric acid; A. CAMPBELL, LAURENE AND CLARK[6] at 20°; B. present work at 23°.

One should point out that both curves in Fig. 3 extrapolate to a solubility for iso-propyl ether in water of ∼ 0.4 g/100 ml, which is appreciably higher than the value quoted by CAMPBELL *et al.*, (shown in the diagram at zero HCl concentration). This effect may be due to a deviation from linearity below approx. 1M hydrochloric acid.

Advantages and limitations of method

The method as described is rapid and easy to use, and gives reproducible results with an overall accuracy, for columns of ether over 1 cm in height, estimated at ± 2%. For smaller amounts of organic solvent this figure becomes larger due to the uncertainty in the correction for the solubility of the solvent in the final neutralized solution. The lower limit of the method is set by this factor and by the necessity to precipitate significant amounts of solvent out of a reasonably small amount of the aqueous phase. One could of course use tubes of much larger total volume to get over this difficulty. The upper limit of the method has not been investigated but will probably be determined by the size of sample necessary to give a column of liquid less than about 4 cm in height. Here again one could no doubt produce a modified centrifuge tube if necessary.

The method is being currently used in solvent extraction investigations and appears especially applicable to the analysis of the third phase which has been found to appear in certain concentrated acid-ether systems[9].

ACKNOWLEDGEMENT

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SUMMARY

A knowledge of the solubility of organic solvents in aqueous solutions of mineral acids is shown to be important in solvent extraction studies. The method described depends upon the direct measurement of the amount of solvent thrown out of the aqueous phase on neutralization. The results of experiments on the solubility of iso-propyl ether in aqueous hydrochloric acid are given. The accuracy, limitations, and uses of the method are discussed.

RÉSUMÉ

Il est important de connaître la solubilité des solvants organiques dans des solutions aqueuses d'acides minéraux, pour l'étude d'extractions au moyen de solvants. Les résultats expérimentaux sur la solubilité de l'éther isopropylique dans l'acide chlorhydrique sont donnés.

ZUSAMMENFASSUNG

Die Kenntnis der Löslichkeit organischer Lösungsmittel in wässrigen Mineralsäuren is wichtig für Untersuchungen über Extraktionsverfahren. Es werden Angaben über die Löslichkeit von Isopropyläther in wässriger Chlorwasserstoffsäure gemacht.

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COLORIMETRIC URANIUM DETERMINATION WITH ARSENAZO*

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Although a large number of reagents have been proposed for the colorimetric determination of uranium, most of these are non-selective and rather insensitive. In several of the methods a preliminary reduction to uranium(IV) is required[1-5]. The reduction step lengthens the procedure and introduces a possible source of error.

Dibenzoylmethane is a sensitive chromogenic reagent for uranium(VI) (the molar absorptivity is around 20,000) and is probably the best of the existing reagents. Although numerous metal ions interfere[6,7], dibenzoylmethane can be made more selective through the use of masking agents. PRIBIL AND JELINEK[8] determine uranium after extracting uranyl dibenzoylmethane from an aqueous EDTA (ethylenediaminetetraacetic acid) solution. Three extractions are required; each involves considerable shaking. BLANQUET[9] has proposed a highly selective method for uranium based on a carbonate precipitation of impurities followed by colorimetric measurement of uranyl dibenzoylmethane in homogeneous solution containing tartrate and EDTA. He does not indicate clearly which of the foreign ions are removed by precipitation and which are masked by the tartrate and EDTA.

Many of the published methods for the determination of small amounts of uranium employ a liquid-liquid extraction, chromatographic separation, electrolysis with a mercury cathode, or other type of preliminary separation. The success of the subsequent colorimetric determination thus depends upon the efficiency of separation. EBELE AND LERNER have reviewed these separative methods[10]. Very recently several other methods have been published that deal with liquid-liquid extractions[11,12] or with ion exchange separations[13].

There are many occasions where a direct, rapid colorimetric determination of uranium without a preliminary separation would be a distinct advantage. The method described in this paper largely fills this need. Arsenazo, 3-(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid, is used as the chromogenic reagent for uranium(VI). This reagent has previously been used for the qualitative detection of several elements[14,15] and for the quantitative determination of aluminum, beryllium, rare earths and zirconium[15-17]. Our determination is carried out entirely in aqueous solution; the color develops rapidly and is stable. The method is applicable to the determination of low concentrations of uranium, and the analysis can be carried out successfully in the presence of moderate quantities of most metal ions. If thorium is present, however, the uranium must be separated by extraction of uranyl diethyldithiocarbamate.

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* Contribution No. 637. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

THE URANIUM–ARSENAZO COMPLEX

In Figs. 1 and 2 the spectral curves of arsenazo and the uranium–arsenazo complex are shown as a function of pH. At pH 8 and below, the wavelength of maximum absorbance is at 595 mμ; at pH 9 and 10 the maximum is shifted toward shorter wavelengths. This wavelength shift, along with the fact that the reagent absorbance at 595 mμ increases significantly above pH 8.5, indicates that the pH for quantitative colorimetric determination of uranium should be below 8.5. In order to establish more precisely the optimum pH range, the absorbance of a uranium–arsenazo solution was measured at 595 mμ as a function of pH. The resulting plot, shown in Fig. 3, indicates that pH 7.0–8.0 is the best for determining uranium with arsenazo.

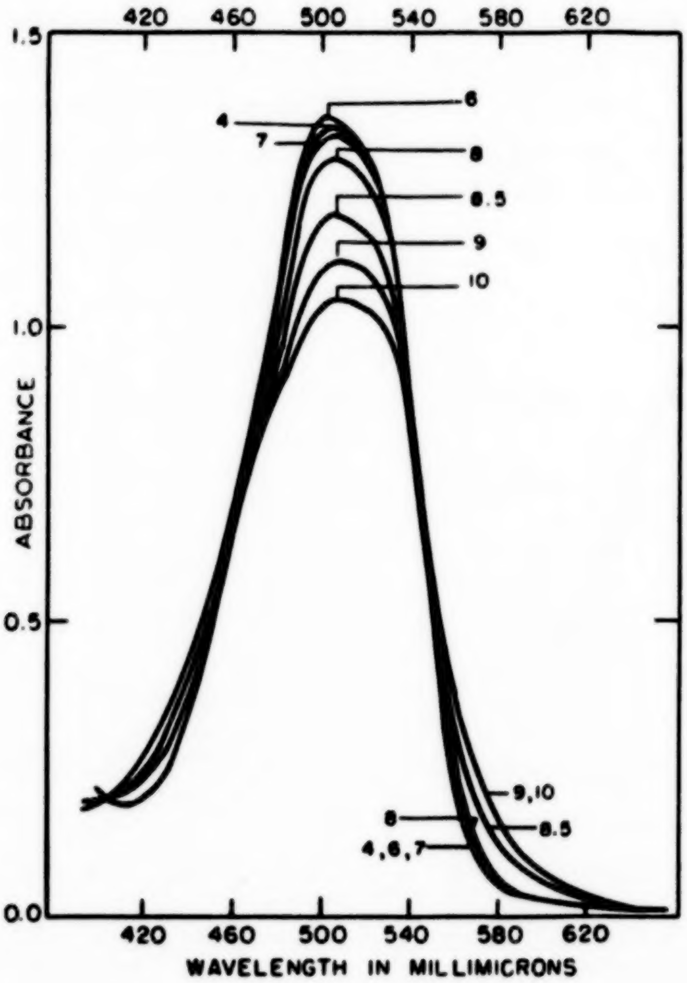

Fig. 1. Spectral curves for arsenazo at pH 4, 6, 7, 8, 8.5, 9 and 10. Solution contained $2 \cdot 10^{-3}$ millimole arsenazo made up to 50 ml. A 1-cm cell was used for spectra.

The ratio of ligand to metal in a metal-organic complex is always of interest. A photometric titration of uranium with arsenazo gave a definite inflection at a mole ratio of arsenazo to uranium of 0.98:1 (see Fig. 4), assuming that the arsenazo was pure acid monohydrate, molecular weight 566. This indicates clearly that a 1:1 complex formed. No evidence was found for any higher complexes. Previously a single 1:1 complex species was found for lanthanum–arsenazo[18].

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The absorbance of uranium solutions complexed with excess arsenazo was measured at pH 7.5, 595 mμ. Beer's law is followed with good precision up to at least 10 ppm of uranium. The solutions were found to be stable for at least 11 days. Accurate determination of the molar absorptivity is complicated by the fact that uncomplexed arsenazo absorbs somewhat at 595 mμ. This can be corrected for by using a measured amount of arsenazo and taking into account the fact that a 1:1 complex is formed.

$$A = A_c + A_r = \varepsilon_c c_c + \varepsilon_r c_r \quad (1)$$

$$c_r = c_r^\circ - c_c. \quad (2)$$

$$A = (\varepsilon_c - \varepsilon_r)c_c + \varepsilon_r c_r^\circ. \quad (3)$$

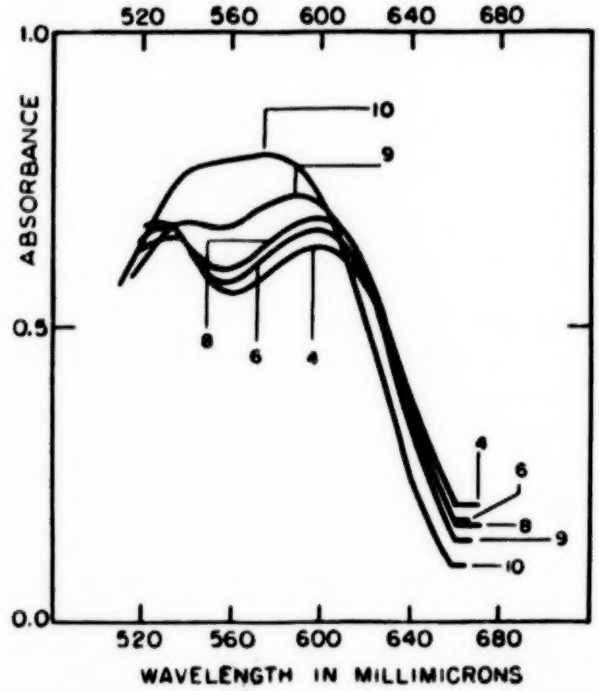

Fig. 2. Spectral curves of uranium–arsenazo complex at pH 4, 6, 8, 9 and 10. Solution contained $7.5 \cdot 10^{-4}$ millimole $UO_2(NO_3)_2$ and $1 \cdot 10^{-3}$ millimole arsenazo made up to 50 ml. A 2-cm cell was used for spectra.

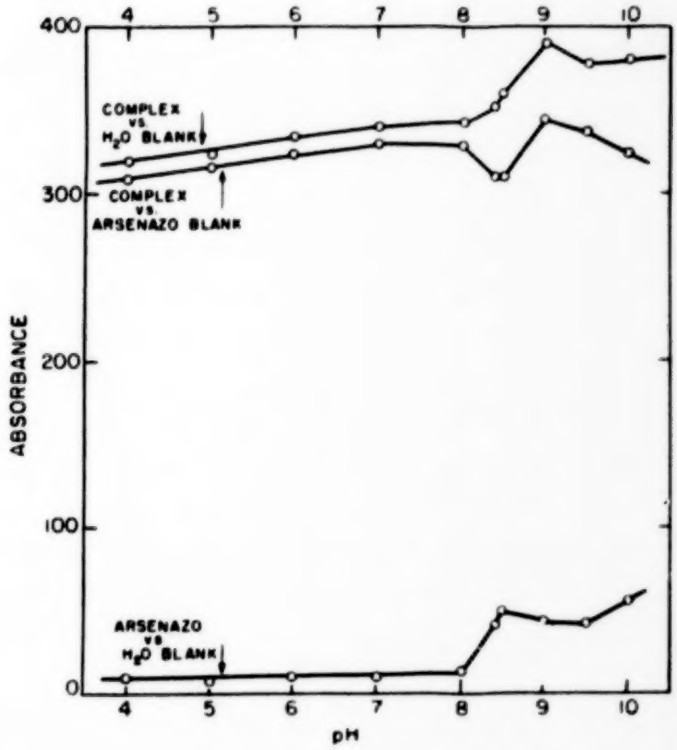

Fig. 3. Absorbance of arsenazo and uranium–arsenazo as a function of pH. Solutions were (1) $7.5 \cdot 10^{-4}$ millimole $UO_2(NO_3)_2$ diluted to 50 ml and (2) $2 \cdot 10^{-3}$ millimole arsenazo diluted to 50 ml. A 1-cm cell was used for all readings.

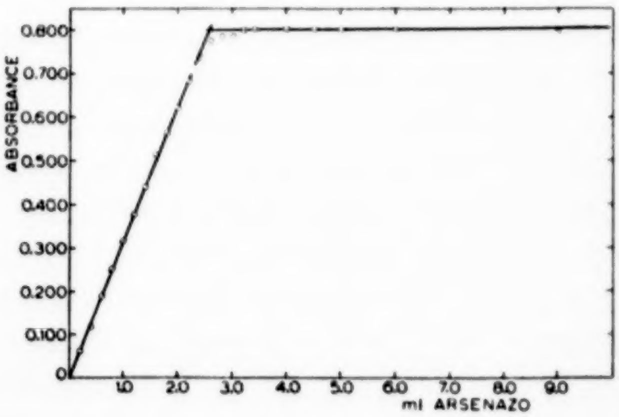

Fig. 4. Photometric titration of uranium with arsenazo $7.5 \cdot 10^{-4}$ millimole of $UO_2(NO_3)_2$ was used. Arsenazo was $2.87 \cdot 10^{-4}M$.

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where subscript c refers to the complex and r to the free reagent; c_r° is the concentration of reagent before complex formation. Plotting A against concentration of uranium gives a straight line with slope equal to $(\varepsilon_c - \varepsilon_r)$ and intercept at zero uranium concentration equal to $\varepsilon_r c_r^\circ$. By this method the molar absorptivity for uranium-arsenazo at 595 mμ and pH 7.5 was found to be 22,900.

INTERFERENCE STUDY

It quickly became apparent that many metal ions would interfere with the simple colorimetric determination of uranium with arsenazo. Thorium and rare earths form an intense violet color with arsenazo over a wide pH range. Iron(III), zirconium(IV) and several divalent metal cations also interfere seriously.

To avoid these interferences, several complexing agents were tried as masking agents. The most widely applicable complexing agent found was EDTA. The addition of EDTA permits the accurate determination of uranium in the presence of at least 35:1 mole ratio of many foreign metal ions to uranium. The data obtained are summarized in Table I.

TABLE I

DIRECT COLORIMETRIC DETERMINATION OF URANIUM IN THE PRESENCE OF ADDED IONS

Ion added	*Masking agent*	*% Uranium recovery*	
		0.005 millimole added ion	*0.025 millimole added ion*
Ag^+	None	—	99.7
Al^{+3}	EDTA	—	98.8
	Acetylacetone	96.9	98.7
Ba^{+2}	EDTA	—	99.1
Be^{+2}	Acetylacetone	102.0	120
Bi^{+3}	EDTA	98.5	100.1
	EDTA	100.4	—
	Thioglycerol	—	100.0
Ca^{+2}	EDTA	98.5	99.1
	EDTA	100.4	—
Cd^{+2}	EDTA	99.0	99.1
	EDTA	99.6	—
Co^{+2}	EDTA	100.0	100.0
	EDTA	104.3	—
Cr^{+3}	EDTA	55.4	—
Cu^{+2}	EDTA	100.0	99.1
	Thioglycerol	101.2	100.0
Dy^{+3}	EDTA	—	101.7
Fe^{+3}	EDTA	98.5	99.4
	EDTA	100.4	—
Hg^{+2}	EDTA	—	99.7
La^{+3}	EDTA	—	97.1
Mg^{+2}	EDTA	—	99.1
Mn^{+2}	EDTA	98.5	99.7
	EDTA	101.2	—
MoO_4^{-2}	Tartaric acid	100.0	99.3
Ni^{+2}	EDTA	98.5	100.6
	EDTA	100.4	—

TABLE I (continued)

Ion added	*Masking agent*	*% Uranium recovery* *0.005 millimole added ion*	 *0.025 millimole added ion*
Pb^{+2}	EDTA	100.0	99.7
	EDTA	103.2	—
Sb^{+3}	Thioglycerol	100.3	100.3
Sc^{+3}	EDTA	—	100.0
Sn^{+4}	EDTA	—	88.3
Sr^{+2}	EDTA	—	99.7
Ti^{+4}	EDTA	100.0	102.6
VO^{+2}	EDTA	—	100.0
VO_3^-	EDTA	99.2	—
WO_4^{-2}	Tartaric acid	100.0	98.7
Y^{+3}	EDTA	—	101.5
Zn^{+2}	EDTA	100.0	100.3
Zr^{+4}	EDTA	101.5	99.7
	EDTA	104.3	—

Uranium taken: 142–178 g
Average recovery (eliminating results more than 10% in error): 99.9%
Standard deviation: ± 1.40%.

The chief limitation of EDTA as a masking agent is that only a slight *excess* of EDTA can be permitted. Up to 0.005 millimoles of EDTA per 50 ml affects the results by an amount that is no greater than the average error in making a colorimetric measurement on the spectrophotometric instrument used. A higher concentration of EDTA causes low results in the uranium determination. Uranium can be determined accurately in the presence of foreign metal ions provided the foreign ions are complexed trongly by EDTA and that the excess EDTA is not greater than 0.005 millimoles per 50 ml. Uranium solutions containing 0.005 millimoles of EDTA per 50 ml follow Beer's law, and we recommend the inclusion of that concentration of EDTA when preparing the standard working curve for uranium.

Complexing agents other than EDTA are useful for masking certain metals. Molybdenum(VI) and tungsten(VI) are effectively masked by tartrate, and titanium(IV) causes only slightly high results in tartrate solution. Uranium can be determined in the presence of aluminum if sulfosalicylate is present. Thioglycerol permits determination of uranium in the presence of antimony, bismuth or copper. A moderate excess of any of these masking agents does not affect the uranium results.

Of the anions studied only phosphate was found to interfere seriously. No interference is caused by 0.2*M* nitrate, chloride, perchlorate or acetate, or by 0.01*M* fluoride, oxalate or sulfate. A 0.2*M* sulfate concentration made the results for uranium only 2.4% low.

EXTRACTION OF URANIUM

Although the direct colorimetric determination of uranium is made selective through the use of masking agents, thorium constitutes a serious interference. For this reason, the preliminary separation of uranium from interfering ions was investigated.

The liquid–liquid extraction of uranyl diethyldithiocarbamate has been reported[19]. If EDTA is added, uranium still extracts quantitatively but the extraction of several other metal diethyldithiocarbamates is prevented. In the presence of EDTA only bismuth, cobalt, copper, mercury, silver and tin diethyldithiocarbamates are extracted along with uranium. The chief value of this extraction, however, is the separation of uranium from metals such as thorium and iron.

After extraction, the problem exists of getting the uranium into a medium suitable for colorimetric determination. Direct measurement of the color of uranyl diethyldithiocarbamate in nonaqueous solution has been employed[19], but this is a rather insensitive method. We have found that back-extraction of uranium into a dilute, aqueous carbonate solution is very quick and satisfactory. The pH of the aqueous solution is then adjusted, arsenazo is added and the absorbance is measured at 595 mμ. Data obtained by this method are presented in Table II.

TABLE II

DETERMINATION OF URANIUM USING EXTRACTION PROCEDURE

Ion added (0.05 millimole)	*% Uranium recovery*	
	0.0023 millimole U	*0.0030 millimole U*
Ag^{+}	98.8	97.6
Al^{+3}	98.0	—
Bi^{+3}	—	95.8
Ca^{+2}	96.8	98.2
Cd^{+2}	99.6	97.6
Co^{+2}	97.6	96.7
Cu^{+2}	99.6	97.0
Fe^{+3}	100.0	98.8
Hg^{+2}	94.8	83.1
Mg^{+2}	100.0	99.1
Mn^{+2}	101.2	97.0
Ni^{+2}	99.2	96.1
Sb^{+3}	96.4	95.8
Sc^{+3}	104.0	100.0
Sn^{+4}	52.4	55.6
Th^{+4} [a]	98.0	100.0
Y^{+3}	98.0	102.0
Yb^{+3}	103.6	97.6
Zn^{+2}	99.6	99.1
Zr^{+4}	99.2	99.1

[a] 0.25 m. mole added.

REAGENTS, SOLUTIONS AND APPARATUS

Arsenazo, 3-(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid. Purify the Eastman Organic Chemicals product by slowly dropping a saturated aqueous solution of arsenazo into an equal volume of concentrated hydrochloric acid. Filter off the orange precipitate, wash with acetonitrile and dry at 110° for 1–2 h. Prepare a 0.001 M aqueous solution from the purified product.

Diethyldithiocarbamate. Prepare a 2% aqueous solution from pure sodium diethyldithiocarbamate. A fresh solution should be prepared every day or two.

EDTA. Prepare a 0.01 M solution from reagent grade disodium or diammonium dihydrogen ethylenediaminetetraacetate.

Sodium carbonate. Prepare a 0.02% solution and adjust the pH to 8.0.

Triethanolamine buffer. Mix equal volumes of 1 M triethanolamine and 0.5 N nitric acid.

Uranyl nitrate. Dissolve an accurately weighed portion of pure U_3O_8 in dilute nitric acid and dilute to the desired volume. A $5 \cdot 10^{-5} M$ solution is convenient for preparing uranium standards.

All other chemicals used were of reagent grade. Metal nitrates or perchlorates were used in the interference study. Demineralized distilled water was used throughout this investigation.

Spectral curves were carried out on a Cary model 12 recording spectrophotometer. All other measurements were made on a Beckman model B spectrophotometer.

PROCEDURES

A. General Colorimetric Procedure

This procedure is for a sample or aliquot containing 5–500 μg of uranium. Dilution and cell size can be adjusted to handle greater or smaller quantities of uranium.

If the sample is highly acidic, adjust the pH to approximately 2 or 3 with sodium or ammonium hydroxide. Add sufficient 0.01 M EDTA to complex foreign metal ions that react with EDTA; do not add more than a 0.5-ml excess of EDTA. If the amount of foreign metal ions present is negligible, add 0.5 ml of 0.01 M EDTA. Add 2 ml of 0.001 M arsenazo solution. Add 5 ml of triethanolamine buffer and dilute to approximately 40 ml. Adjust the pH to 7.5 with dilute nitric acid or ammonium hydroxide, transfer to a 50-ml volumetric flask and dilute to volume. Measure the color against a reagent blank (a water blank may be used) at 595 mμ in a 1-cm cell. Calculate the uranium concentration with the aid of a Beer's law plot previously prepared using this same procedure.

If aluminum may be present, it is advisable to heat the solution to boiling after adding the EDTA. If molybdenum (VI), tungsten(VI) or titanium(IV) may be present, add 1 ml of 0.1 M tartaric acid to the acidic sample before continuing with the rest of the procedure. These metals are not complexed by EDTA under the conditions of the determination.

B. Extraction Procedure

To a sample containing not more than 0.08 millimole of foreign metal, add 2 ml of 0.05 M EDTA and approximately 1 ml of pyridine. Dilute to approximately 20 ml, add 3 ml of 2% diethyldithiocarbamate and adjust the pH to 7–8.* Transfer without delay to a separatory funnel and extract with 25 ml of chloroform. A few ml of a saturated solution of $NaNO_3$ may be added to clear up the layers. Drain the chloroform layer into another separatory funnel which contains 50 ml of 0.02% sodium carbonate. Add 1 ml of additional diethyldithiocarbamate solution to the aqueous layer and re-extract with 15 ml of chloroform. Drain this chloroform layer into the same sodium carbonate solution, then shake the carbonate and combined chloroform extracts for 30 seconds to back-extract the uranium. Drain the chloroform from this back-extraction into another separatory funnel and back-extract with a second 25-ml portion of sodium carbonate solution. To combined carbonate solutions, add 1 ml of concentrated perchloric acid to destroy the carbonate. Then add 5 ml of triethanolamine buffer, 5 ml of 0.001 M arsenazo and adjust the pH to 7.5. Dilute to exactly 200 ml and measure the color at 595 mμ.

SUMMARY

A rapid and sensitive method is described for the quantitative colorimetric determination of uranium(VI). Masking agents such as EDTA, tartaric acid or thioglycerol make possible the determination of uranium in the presence of many foreign metal ions. If thorium is present, a preliminary extraction of uranium as the diethyldithiocarbamate is required.

RÉSUMÉ

Une méthode rapide et sensible est décrite pour le dosage colorimétrique de l'uranium(VI). Des réactifs de masquage permettent le dosage en présence de nombreux ions étrangers. En présence de thorium, on doit procéder à une extraction préliminaire de l'uranium sous forme de diéthyldithiocarbamate.

ZUSAMMENFASSUNG

Es wird eine empfindliche Schnell-Methode für die colorimetrische Bestimmung von Uran-(VI) beschrieben. Fremdmetalle können mit EDTA usw. maskiert werden. Bei Gegenwart von Thorium muss das Uran als Diäthyldithiocarbamat durch Extraktion abgetrennt werden.

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* If thorium is the interfering ion, let the solution stand for 15–30 min at pH 7–8 before adding the diethyldithiocarbamate solution.

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RESORCINOL AS AN ANALYTICAL REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM

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In recent years a number of organic reagents have been suggested for the colorimetric estimation of uranium(VI), for example, dibenzoylmethane[1], salicylic acid[2], sulphosalicylic acid[3], salicylamide[4], salicylamidoxime[5], etc. Of these dibenzoylmethane is claimed to be the most sensitive reagent known so far, but it has the disadvantage of being insoluble in water. Resorcinol produces an orange-red coloration with uranyl salts, which colour reaction was first observed by Seimssen[6]. Resorcinol is extremely soluble in water, easily available and cheap. In view of these advantageous properties, resorcinol was tested as a reagent for the spectrophotometric determination of uranium, and the results are described in this paper.

EXPERIMENTAL

Absorption measurements were made on Coleman's Universal Spectrophotometer, Model 14. A Marconi pH meter was employed for pH measurements, a glass electrode and a saturated calomel reference electrode being used. A freshly prepared solution of resorcinol (Merck's pure quality) was always used for the measurements. A stock solution of uranyl acetate ($UO_2(CH_3COO)_2 \cdot 4H_2O$, a Swiss pure sample) was made by dissolving about 10 g per litre; the uranium content was standardised gravimetrically by precipitating with ammonia and igniting the precipitate to U_3O_8.

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DISCUSSION

The absorption spectra of the coloured species ($M/70$ uranyl acetate and $M/7$ resorcinol in water) in presence of excess of resorcinol at pH 4.72 is shown in Fig. 1, along with that of pure reagent of the same concentration at pH 5.68. It follows from the graph that the coloured product has high absorption between 400 mμ and 450 mμ, whereas the reagent has comparatively negligible absorption. Therefore the wavelength 400 mμ was selected for the absorption measurements to investigate the various factors mentioned below.

Colour intensity

Solutions containing the same concentrations of uranium, and resorcinol (in excess), were made at different pH values and their absorption was measured at 400 mμ. The results, which are shown in Fig. 2, indicate that the colour intensity reaches a maximum at pH 4.72 and then decreases at higher pH values. It can further be observed that excess of reagent, even more than a ten-fold excess, has no influence on the colour intensity.

Beer's law

The validity of Beer's law for the system was investigated by the usual method at 400 mμ. The plot of the values of log T against concentration is shown in Fig. 3. This figure indicates that the system obeys Beer's law in the concentration range from $1.125 \cdot 10^{-3} M$ to $0.25 \cdot 10^{-3} M$.

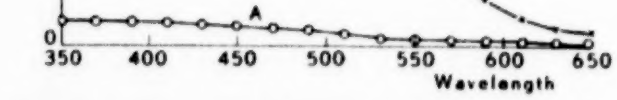

Fig. 1. Curve A: Absorption of an aqueous solution of resorcinol $M/7$. Curve B: Absorption of a mixture of uranyl acetate $M/70$ and resorcinol $M/7$ in water.

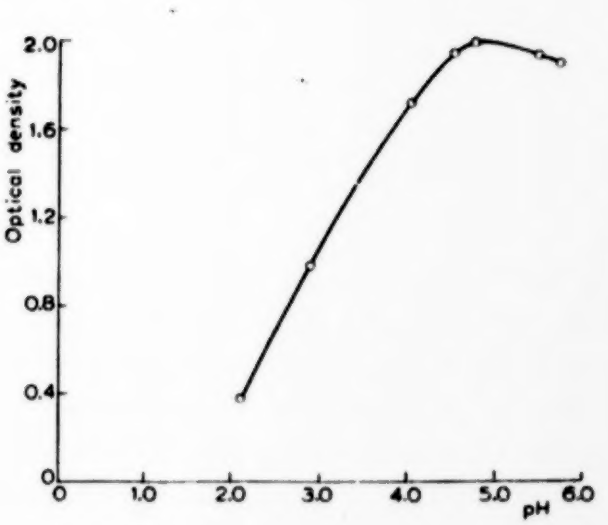

Fig. 2. Variation of optical density with pH of a mixture of uranyl acetate $M/70$ and resorcinol $M/7$ in water.

Stability of the colour and the sensitivity of the reagent

The coloured product remained stable at room temperature and there was no change in the optical density even after 48 h. The sensitivity of the reagent is approximately $M/32{,}000$ (7.43 p.p.m.) of UO^{+2} ion in excess of resorcinol.

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Composition

The composition of the product was determined by following JOB's continuous variation method as modified by VOSBURGH AND COOPER[7]. For this investigation uranyl acetate *M*/40 and resorcinol *M*/20 were used. These solutions were mixed in different proportions keeping the total volume the same (20 ml). The results of the optical density measurements are plotted against $\frac{[R]}{[R] + [UO_2^{+2}]}$ in Fig. 4. The curve shows that maximum optical density (1.2) is obtained when $\frac{[R]}{[R] + [UO_2^{+2}]}$ equals 0.66, indicating the formation of a 1:2 product between UO_2^{+2} ion and the reagent. An attempt was made to determine the composition of the coloured product by conductivity and pH titration methods, but these failed to give any conclusive results, possibly owing to the fact that the uranyl resorcinolate formed is highly dissociated in solution and that one of the constituents of the reaction product is a free acid:

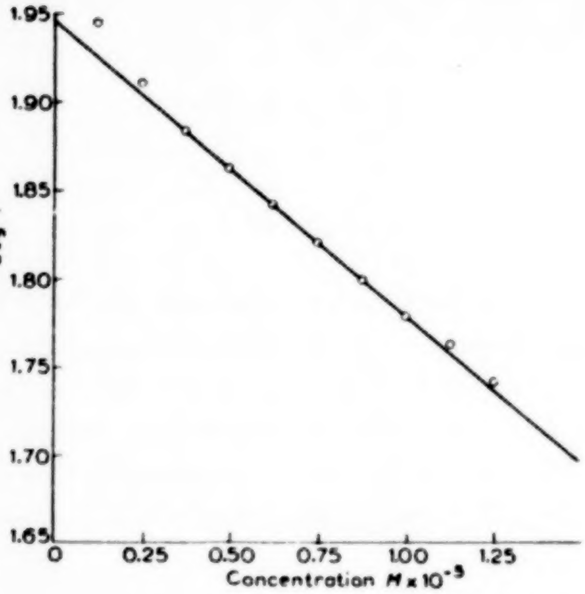

Fig. 3. Curve showing the validity of Beer's law for the system uranyl acetate and resorcinol.

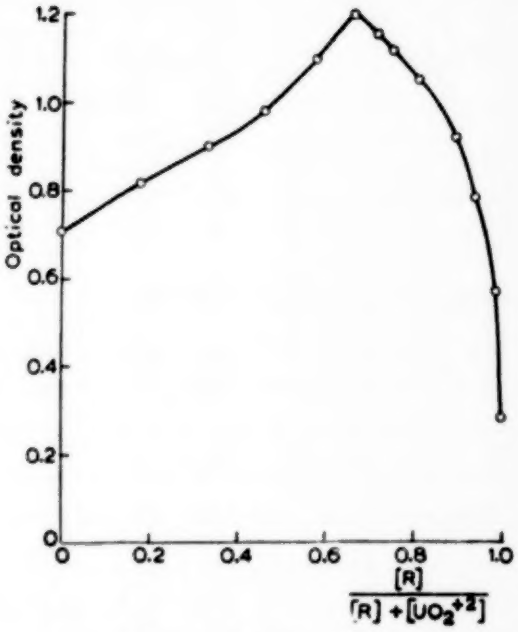

Fig. 4. Curve showing the composition of the coloured product formed from uranyl acetate and resorcinol.

$$UO_2(CH_3COO)_2 + 2C_6H_4(OH)_2 \rightleftharpoons UO_2(C_6H_5O_2)_2 + 2CH_3COOH$$

Interference of other ions

The effect of certain cations and anions that are likely to interfere with the estimation of uranium was investigated and the results are summarised in Table I. The amount of an ion (in p.p.m.) that will produce ± 2% change in optical density was taken as the tolerance limit.

ACKNOWLEDGEMENT

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TABLE I

EFFECT OF SOME CATIONS AND ANIONS

10.0 ml *M*/800 uranyl acetate + 8.0 ml *M*/64 resorcinol + 2.0 ml water; total volume 20.0 ml.

Salts	*Ions*	*p.p.m.*	*% change*	*Tolerance limit p.p.m.*
K_2SO_4	SO_4^{-2}	10,000	no change	large excess
KNO_3	NO_3^-	20,000	—2	20,000
KCl	Cl^-	10,000	—1.5	15,000
CH_3COONa	CH_3COO^-	3	+4	7
		9	+1.3	
NaF	F^-	10	—25	—
		8	—8	
NaK tartrate	$C_4H_4O_6^{-2}$	24	—22	—
$NaBO_2$	BO_2^-	4	+3	2
		8	+12	
Na_2CO_3	CO_3^{-2}	5	+2	5
		12	+6	
Na citrate	$C_6H_5O_9^{-3}$	20	—32	—
Na_2WO_4	WO_4^{-2}	62	—1.4	72
		37	+6	
NH_4 molybdate	MoO_4^{-2}	18	+8	—
		2	+5	
NH_4VO_3	VO_3^-	1	+48	13
		5	+1	
$K_2Cr_2O_7$	$Cr_2O_7^{-2}$	10	+12	—
Na_2HPO_4	PO_4^{-3}	6	—1.5	8
		15	—5	
$CoCl_2$	Co^{+2}	1	+2	1
$MnCl_2$	Mn^{+2}	1	—12	—
$Ce(NO_3)_4$	Ce^{+4}	1	—9	—
$FeCl_3$	Fe^{+3}	2	+3	1
		3	+5	
$Th(NO_3)_4$	Th^{+4}	1	+2	1
		2	+4	
$CuCl_2$	Cu^{+2}	1	—1	—
		2	+1	
$CrCl_3$	Cr^{+3}	1	—1.8	1
		2	—21	

SUMMARY

A spectrophotometric study of the reaction of uranyl acetate and resorcinol shows that an orange-red coloured resorcinolate of composition 1:2 is formed. This colour reaction can be conveniently used for the spectrophotometric estimation of uranium at pH 4.72.

RÉSUMÉ

Une méthode spectrophotométrique est proposée pour le dosage de l'uranium au moyen de résorcinol. Le composé obtenu est rouge orange.

ZUSAMMENFASSUNG

Uranylacetat gibt mit Resorcin eine orangerot gefärbte Verbindung, die zur spektrophotometrischen Bestimmung des Urans verwendet werden kann.

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THE SPECTROPHOTOMETRIC DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS

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Until the microgram method[1] of separation of polycyclic aromatic hydrocarbons by elution chromatography on alumina columns was devised, the presence of this class of compound in small proportions could not readily be demonstrated; but since that time, improvements in separation methods and in ultra-violet and fluorescence spectrophotometry have made possible more rapid qualitative and quantitative analyses. The object of the present paper is to describe some recent advances and improvements in technique and to present tabulated essential information covering a wider range of compounds than has previously been given. This should be of use in the analysis of combustion or pyrolysis products such as smokes and soots and tars.

The proportions of polycyclic aromatic hydrocarbons in such products is usually small; very often only a few parts per million. It follows therefore that a satisfactory analytical method must comprise (*i*) a quantitative separation process of extremely small amounts of the wanted material from the rest of the very complex mixture and (*ii*) a sensitive method of identification and determination in the separated fraction.

The use of elution chromatography from alumina columns followed by ultraviolet and fluorescence spectrophotometry has been previously shown in this Department to fulfil these requirements and to be suitable for a wide range of combustion products[2-5]. Earlier workers on chromatographic separation of polycyclic aromatic hydrocarbons[6-11] were more interested in preparative separations and purifications than analysis and had no need to standardize the activity of the alumina or to ensure complete recovery of their products. In the first quantitative work carried out in this laboratory it was customary to select partially de-activated alumina and to employ this material for the separations. Such materials were not wholly satisfactory as they could be standardized only for the duration of the supply of de-activated alumina and thus the methods were not repeatable when the supply had been used. Throughout this paper the separations described were effected on alumina previously brought into equilibrium with water vapour over 75% sulphuric acid[12] in order to ensure reproducible conditions.

The method used by COOPER[13] has given good service for relatively "clean" specimens such as soots and air solids, but has frequently failed to reveal suspected constituents in complex materials such as condensed tobacco smoke. With such samples it is almost always necessary to recombine chromatographic fractions in groups and to pass them through additional columns. In these circumstances the use of an automatic recording spectrophotometer (such as the Beckman D.K. 2) is of great advantage because of its rapid working; and it is now customary to prepare with this apparatus a spectrum of every chromatographic fraction to assist in preliminary identification of constituents and thus to aid the choice of fractions for subsequent re-chromatography. Manual plotting of complete spectra, as was done in the original method[2], for each fraction is impossibly time consuming when many samples have to be analysed.

EXPERIMENTAL

As the method is so sensitive (as little as 0.01 μg of pyrene in 1 ml of solution can be recognised) special care has to be taken to clean all apparatus and to purify all materials.

Cleaning of glassware

All glassware was cleaned by immersion in chromic acid solution, washing with water and drying in an electric oven. This cleaning was completed just before use to avoid possible contamination by atmospheric pollutants.

Preparation of solvents

Spectrophotometrically pure solvents for this work were prepared by distilling the purest commercially available material through glass apparatus using a short column of glass marbles to prevent contamination of the distillates by spray. When cyclohexane was required free from benzene, it was allowed to flow through a column of silica gel (150 × 5 cm) freshly activated by heating to 300°.

Preparation of alumina columns

Active alumina (Peter Spence, type H, 100 to 200 mesh) was used for all this work. It was brought to standardized activity and used by the method previously described[12].

Chromatographic sequence

The most complete list of polycyclic aromatic hydrocarbons with their chromatographic sequence for elution from alumina columns was published by COOPER AND WEDGWOOD[14]. This list and that in Table I, were the result of experiments with mixed solutions of pure hydrocarbons in cyclohexane and they hold for quantities of the order of several micrograms of each compound per ml of solution. In the presence of other compounds and with considerably different amounts of the hydrocarbons this order may be disturbed. It has sometimes been found profitable to employ displacement carriers to space out the hydrocarbons in the chromatographic sequence[3].

Determination of absorption spectra

Standard solutions were prepared by weighing the pure hydrocarbon dissolving in cyclohexane and diluting to a known volume. Absorption peak wavelengths were determined by direct reference to the wavelength scale of the instrument which was calibrated by means of the hydrogen lines at 4861 Å and 6536 Å, and by means of the spectrum of pure benzene in cyclohexane. In Table I also are listed the wavelengths of these absorption maxima to the nearest mμ. To assist in identification of compounds in spectra of unknown mixtures these compounds could be listed against the wavelengths.

Quantitative analysis

For the determination of compounds in solution by means of their absorption spectra a number of empirical techniques have been employed. All these depend upon the solution obeying Beer's law over the range of concentrations employed. COOPER[13] used a "base line" technique in which he drew a tangent to the minima at each side of the maximum absorption and measured the height from this line. GILBERT[15] and others used to measure the absorbance at the maximum and at a fixed wavelength difference above and below the maximum. The difference between the mean of these and the maximum absorbance was regarded as being proportional to the quantity of compound under investigation. These techniques have been tested on a number of compounds but are of necessity less accurate than absorbance measurements because smaller heights are measured. In GILBERT's method errors may be introduced by the asymmetry of absorption peaks. Fig. 1 shows that for serial dilutions of cyclohexane solutions of anthracene, pyrene and 3:4-benzpyrene all three techniques are useful. Similar results are given with other hydrocarbons.

For quantitative determinations it is best to calibrate the spectrophotometer with standard solutions and to prepare a table of factors (absorbances per microgram per ml) to convert the absorbances of the test solution into concentrations. Any of the arbitrary methods described above may be used for this purpose but total absorbance measurements are the most accurate. Table I gives a list of these calibration factors, and wavelengths recommended for quantitative work (underlined).

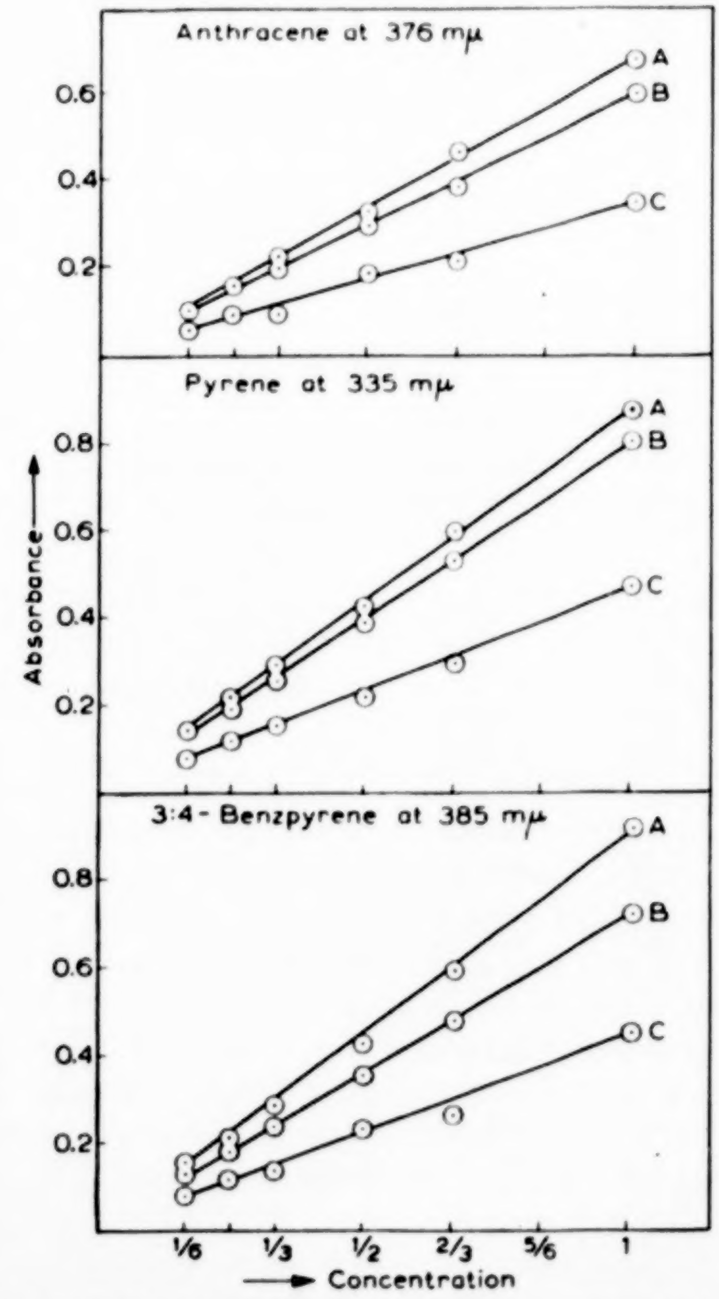

Fig. 1. Concentrations–calibration relationship for anthracene, pyrene and 3:4-benzpyrene, 13.32, 2.95 and 7.22 μg/ml respectively, each diluted to 2/3, 1/2, 1/3, 1/4 and 1/6 of the original concentration. *A* = total absorbance, *B* = absorbance measured from base of peak, *C* = absorbance from base line + or — 3mμ from peak.

TABLE I

CHROMATOGRAPHIC SEQUENCE OF ELUTION OF POLYCYCLIC AROMATIC HYDROCARBONS FROM ACTIVE ALUMINA COLUMNS WITH CYCLOHEXANE

Compound	*Wavelength of peaks*	*Absorbance (μg/ml)*
Naphthalene	297	0.00283
	301	0.00239
	304	0.00179
	306	0.00168
	311	0.00212
	320	0.000135
Azulene	296	0.0365
	315	0.0171
	322	0.0236
	327	0.0275
	337	0.0348
	341	0.0413
	353	0.00816
2-Methylnaphthalene	305	0.00315
	312	0.00193
	320	0.00326
Acenaphthene	280	0.0398
	288	0.0445
	300	0.0287
	307	0.0189
	310	0.000907
	314	0.000544
	321	0.0110
Acenaphthylene	276	0.0200
	311	0.0504
	323	0.0627
	335	0.0304
	340	0.0307
Fluorene	221	0.109
	265	0.129
	290	0.0423
	294	0.0348
	301	0.0661
Phenanthrene	252	4.13
	275	0.883
	282	0.681
	293	0.897
Anthracene	253	1.24
	325	0.00704
	340	0.0122
	357	0.0264
	376	0.0358
Pyrene	273	0.295
	306	0.588
	320	0.161
	335	0.302
Fluoranthene	237	0.281
	254	0.0815
	259	0.0653
	263	0.0747
	272	0.0602
	277	0.127
	282	0.0965
	288	0.265
3-Methylpyrene	233	0.214
	243	0.373
	254	0.0491
	260	0.0552
	266	0.129
	276	0.268
	313	0.0569
	327	0.136
	344	0.214
	355	0.00869
1:2-3:4-Dibenzanthracene	323	0.0328
	333	0.0260
	350	0.0123
	375	0.00222
1:2-Benzanthracene	250	0.241
	255	0.279
	260	0.205
	269	0.183
	278	0.354
	289	0.460
	300	0.0435
Chrysene	269	0.755
	282	0.0617
	294	0.0612
	306	0.0661
	320	0.0664
Naphthacene	270	1.08
	294	0.133
	374	0.00465
	393	0.105
	413	0.0228
	441	0.0443
	471	0.0495

TABLE I (Continued)

Compound	*Wavelength of peaks*	*Absorbance (µg/ml)*
Perylene	253	0.195
	339	0.0150
	355	0.0228
	388	0.0461
	409	0.0993
	437	0.139
1:2-Benzpyrene	257	0.109
	267	0.130
	278	0.179
	290	0.246
	317	0.104
	332	0.167
3:4-Benzpyrene	266	0.213
	273	0.134
	285	0.201
	297	0.297
	331	0.0240
	347	0.0584
	364	0.107
	385	0.126
	404	0.0173
1:12-Benzperylene	249	0.0747
	255	0.0883
	261	0.0823
	276	0.0895
	289	0.151
	300	0.210
	313	0.0174
1:12-Benzperylene (continued)	392	0.0232
	345	0.0346
	363	0.0743
	384	0.0985
Anthanthrene	233	0.312
	259	0.138
	294	0.142
	307	0.325
	380	0.0445
	401	0.115
	406	0.132
	422	0.160
	430	0.284
Coronene	302	0.818
	317	0.0667
	324	0.0797
	334	0.0670
	339	0.195
	345	0.0424
3:4-9:10-Dibenzpyrene	223	0.136
	234	0.149
	242	0.319
	272	0.124
	283	0.181
	295	0.285
	314	0.0913
	330	0.0799
	354	0.0723
	372	0.194
	394	0.298

APPLICATION OF THE METHOD

The procedure adopted in the analysis of combustion products for polycyclic aromatic hydrocarbons depends very much upon the type of specimen. The method has been successfully used for materials of many kinds including carbon blacks, soots, urban air solids, condensible smokes in which the disperse phase is a liquid or semi solid (tobacco smoke, wood smoke and coal tar are examples of this), thermal decomposition or pyrolysis products (which may vary from dry soots to dark mobile liquids) and other materials which have through accident or design been subjected to the action of smokes or other combustion products (in this category can be included urban vegetation, soil, tobacco, snuff, smoked foods and surface drainage water containing no industrial effluents). It has also been used in the investigation of carbon formation in flames, especially reversed hydrocarbon flames.

In some cases a great deal of the specimen is either aqueous or hydrophilic (tobacco smoke and wood smoke are in this class). Such materials are easily dissolved in acetone, the solution is then mixed with an equal volume of cyclohexane and the mixture distilled until the temperature of the vapour reaches 70°. The cooled solution is then poured off from the aqueous layer (often semi-solid at this stage) and the process repeated several times. Smoked foodstuffs, especially meats may give considerable difficulty because of the presence of fats. These are best hydrolysed with alcoholic sodium hydroxide and then extracted with cyclohexane. Stubborn emulsions may be formed at this stage but in most cases can be broken by adding quantities of calcium chloride.

When a clear cyclohexane solution has been prepared it is extracted in turn with several quantities of dilute sulphuric acid, water and sodium hydroxide. It may then be submitted to chromatographic separation as described earlier. Solutions in cyclohexane for chromatography should be dry. In most cases a single column treatment is enough, but with tobacco smoke a preliminary separation is necessary.

The degree of adsorption of the hydrocarbons from cyclohexane solution upon alumina varies very much from the least strongly held, naphthalene, to coronene. This results in a very slow elution of the hydrocarbons later in the sequence and consequently very dilute later fractions. The use of a solution of benzene in cyclohexane for eluting later fractions increases the concentration but introduces strong light absorption below 260 mμ. As an alternative method, it has been found useful to employ two columns for separate aliquots of the solution in cyclohexane; one, brought to equilibrium with 70% sulphuric acid for the upper members of the sequence and the other in equilibrium with 50% sulphuric acid for the remainder. With heavy general light absorption the use of the calibration factors given in Table I may be inaccurate. In such cases and indeed in any work which needs confirmation of identity and quantity, the addition of a standard solution of one of the constituents as an internal standard is a great advantage.

ACKNOWLEDGEMENT

The author thanks the Medical Research Council for supporting this investigation by the loan of equipment and provision of technical assistance.

SUMMARY

The determination of polycyclic aromatic hydrocarbons by elution chromatography from alumina columns followed by ultra-violet spectrophotometry has been elaborated for a more extended range of substances than has been published previously. The methods have been standardised and tables of absorption peaks are provided for easy identification of a number of compounds commonly found as traces in combustion products. Recommendations are given for the preparation of samples for determinations by this method, which has been successfully employed for the analysis of carbon blacks, soots, urban air solids, condensible smokes such as tobacco smoke, wood smoke and coal tar, thermal decomposition or pyrolysis products and other substances, such as urban vegetation, soil, tobacco, snuff, smoked food, and surface drainage water, which have been subjected to the action of smokes or other combustion products.

RÉSUMÉ

Une méthode est proposée pour le dosage des hydrocarbures aromatiques polycycliques par chromatographie et spectrophotométrie dans l'ultra-violet. Ce procédé a pu être appliqué avec succès à l'analyse de suies, de poussières, de fumées, de produits de décomposition thermique et d'autres substances exposées à des fumées ou à d'autres produits de combustion.

ZUSAMMENFASSUNG

Es wird eine chromatographische und UV-spektrophotometrische Methode zur Bestimmung von mehrkernigen aromatischen Kohlenwasserstoffen beschrieben. Diese Methode wurde mit Erfolg

bei der Untersuchung von Russ, Rauch und sonstigen Verbrennungsprodukten, oder bei Substanzen, die mit Verbrennungsprodukten in Berührung kamen, angewandt.

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THE DETERMINATION OF MAGNESIUM IN THE PRESENCE OF LARGE AMOUNTS OF ZINC

A SPECTROPHOTOMETRIC METHOD

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INTRODUCTION

The aim of the investigation, described in this paper, was to develop a method for the determination of 100–1000 μg of magnesium in the presence of 1 g of zinc and small amounts of other metals, such as manganese, iron, nickel, aluminium, lead and calcium.

It is advantageous to keep the amount of zinc as small as possible, since it may be expected that in the case of a large amount of zinc with respect to magnesium the first metal will have to be removed in order to eliminate interference of the magnesium determination. It is then desirable to use a spectrophotometric method for the determination of magnesium. This method should have a high sensitivity.

For this spectrophotometric determination some methods have already been described in the literature. A reagent widely used for this purpose is titan yellow, which forms a colour lake when adsorbed on colloidal magnesium hydroxide[1,2,3]. Other reagents that can be used are Eriochrome Black[4,5] and 8-hydroxyquinoline[6]. Recently, Mann and Yoe have described procedures based on the formation of coloured compounds of magnesium with sodium 1-azo-2-hydroxy-3-(2,4-dimethylcarboxanilido)-naphthalene-1′-(2-hydroxybenzene-5-sulphonate)[7] and with 1-azo-2-hydroxy-3-(2,4-dimenthylcarboxanilido)-naphthalene-1′-(2-hydroxybenzene)[8].

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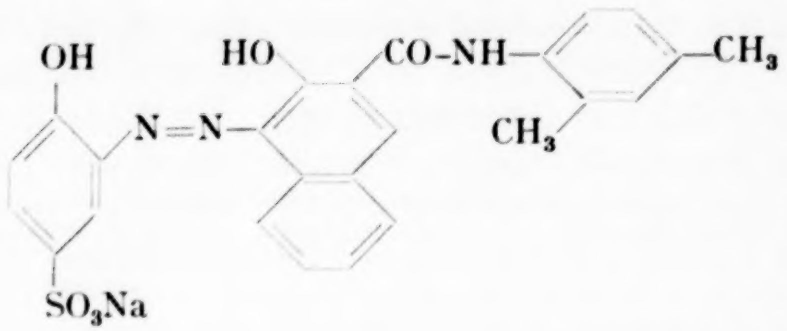

The coloured complex of magnesium and the second reagent is formed in ethanolic medium. Although calcium does not form a coloured complex with the reagent, it may interfere owing to precipitation of its salts in the ethanolic solution. When the second reagent is used there is a greater tolerance for water than when the first one is used. It is obvious that when more water is tolerated the possibility of precipitation of calcium salts decreases. For this reason the authors mentioned prefer the second reagent to the first one. Of course, the possible interference of calcium depends upon the anions present. The sensitivity of the method is high. According to MANN AND YOE[8] a solution of the coloured magnesium complex containing 20 μg of magnesium per litre has an absorbance of 0.020 when measured in 1-cm cells at 505 mμ. The coloured complex is formed at pH = 8.95. A disadvantage of the method is that it is necessary to prepare a new calibration graph for each freshly prepared reagent solution.

Because of this high sensitivity, it was decided to study the applicability of the method to the determination of magnesium in the presence of large amounts of zinc. The fact that heavy metals in amounts of the same order of magnitude as that of magnesium or larger, interfere with the method should not be considered as a specific disadvantage, since these metals also interfere in other procedures.

MANN AND YOE[7] found that a chloroform extraction with 8-hydroxyquinoline can be used for the removal of these metal ions. However, the amounts of metals that can be removed in this way are limited to about one milligram. This means that in our case where so much zinc must be removed, another method of separation had to be found.

A known method for the removal of several heavy metal ions from an aqueous solution is mercury cathode electrolysis. WIBERLEY AND BASSET[9] used this separation technique in the determination of aluminium in steel. These authors used a cell according to MELAVEN[10] which was slightly modified. After this electrolysis, aluminium, calcium and magnesium remain in the solution. Besides these metals titanium, zirconium and vanadium are not removed.

This method of separation was thought to be attractive and it was therefore decided to investigate this separation method combined with the procedure proposed by MANN AND YOE[8], in order to solve our problem.

EXPERIMENTAL

Preliminary experiments

A calibration graph was prepared according to the procedure recommended by MANN AND YOE[8], starting from solutions that contained known amounts of magnesium. All other metals were absent. Five different amounts of magnesium were taken and for each three separate determinations were carried out. The graph, which is not a straight line, is given in Fig. 1.

The numerical values are given in Table I. In this Table the amount of magnesium is the amount in the final solution of which the absorbance is measured.

TABLE I

Magnesium present μg	*Absorbance*		
2	0.065	0.067	0.067
4	0.114	0.115	0.112
6	0.162	0.160	0.161
8	0.196	0.194	0.192
10	0.219	0.220	0.220

In order to establish the precision of the method, the equation of the calibration graph was calculated from the absorbances by the method of least squares. A quadratic relationship was supposed to hold. With the aid of this equation the standard deviation of a single determination, *i.e.* the standard deviation of an amount of magnesium predicted from a measured absorbance using the graph, was calculated. We found $s = 0.16$ μg of magnesium and therefore conclude that the precision of the method is fair.

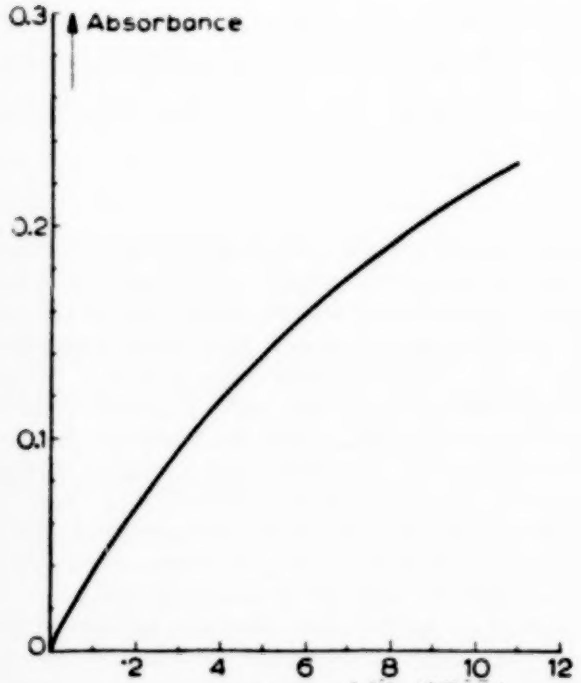

Fig. 1. Calibration graph for the determination of magnesium according to MANN AND YOE[8].

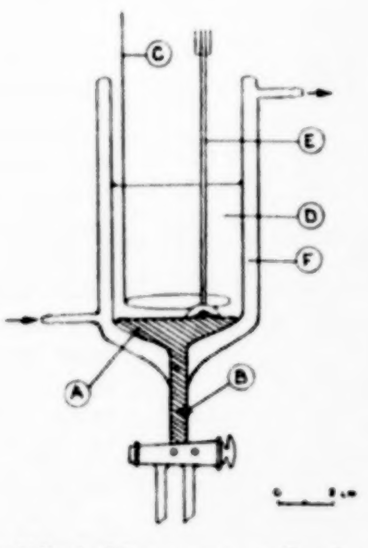

Fig. 2. Modified MELAVEN cell. A: mercury cathode; B: platinum wire; C: anode, platinum wire 1.5 mm ø; D: sample solution; E: stirrer; F: cooling water.

The removal of zinc from an aqueous solution by mercury cathode electrolysis was also studied. In these experiments we started from zinc sulphate, to which small amounts of magnesium, aluminium and calcium were added. A modified MELAVEN cell, as shown in Fig. 2, was used.

From a few experiments it followed that 400 mg of zinc can be quantitatively removed from an acidified solution by electrolysis for 30 min, using a current of 5 A.

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After this period no zinc could be detected in the solution by means of the reaction with potassium ferrocyanide. During the electrolysis the solution was stirred with an air-driven stirrer according to STOCK AND FILL[11].

The solution obtained in this way is strongly acid. According to MANN AND YOE[8] the solution in which magnesium is to be determined should be slightly acid. A large amount of acid must therefore be removed from the solution. It was established that this could not be done by a simple neutralization with alkali hydroxide, since the alkali salt so formed unfavourably influences the results of the magnesium determination. Therefore, the acid had to be eliminated in another way. The usefulness of some anion exchangers for this purpose was studied .The slightly basic anion exchanger Dowex 3 was found to be quite suitable. After passing the electrolysed solution through a column packed with this exchange resin it was established that no magnesium was retained by the resin. The solution to be passed through the column must be dilute with respect to magnesium, in order to prevent losses by precipitation of magnesium hydroxide in the column. Poor results were obtained with the anion exchangers Dowex 2 and Amberlite IR4B, because part of the magnesium present was retained by the resin. This phenomenon could not be decreased by heating the solution and the washing water to about 50°.

It proved to be necessary to treat the solution obtained after anion exchange with 8-hydroxyquinoline in chloroform as proposed by MANN AND YOE[7], in order to remove aluminium. Use is then made of the fact that aluminium 8-hydroxyquinolate can be quantitatively extracted from an aqueous solution with chloroform at pH between 5 and 6.7, while magnesium 8-hydroxyquinolate is not formed at pH values under 6.7.

Based on these experiences the following procedure was developed.

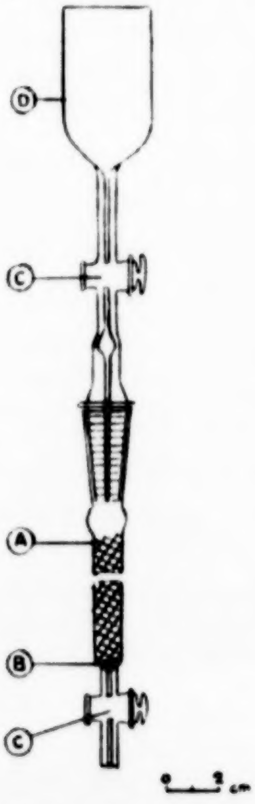

Fig. 3. Ion-exchange apparatus. A: resin column; B: glass wool plug; C: 1-mm capillary stopcocks; D: introductory funnel.

Procedure

Transfer 25 ml of a neutral zinc solution containing 400 mg of zinc as zinc sulphate and 40–400 μg of magnesium into the electrolysis cell (Fig. 2), which contains 15 ml of mercury. Acidify with 3 ml of $4N$ sulphuric acid and dilute with water to about 50 ml, so that the solution is about $0.25N$ in sulphuric acid. Cool the cell with running water, start the stirrer, which is positioned so that only the top layer of mercury is agitated, cover the cell with a split watch-glass to prevent spray losses and electrolyse the solution for 30 min, using a current of 5 A for which 12–18 V is required. Draw off the mercury layer without interrupting the current, and pass the aqueous solution through a column (Fig. 3) packed with Dowex 3 at a rate of one drop per second, collecting the effluent in a 200-ml volumetric flask.

Wash the column with 100 ml of water, and combine washings and effluent. Make this solution just acid to neutral red (pH: 6, 7) and dilute with water to the mark. From this solution pipette 50 ml into a separatory funnel, add 5 ml of 5% 8-hydroxyquinoline in chloroform, shake vigorously and draw off the chloroform layer. Repeat this extraction four times and finally extract the aqueous solution with two 2-ml portions of chloroform. Transfer the aqueous solution to a 100-ml volumetric flask and dilute with water to the mark.

From this solution pipette 10 ml into a 25-ml volumetric flask containing 5 ml of a 0.01% solution of 1-azo-2-hydroxy-3-(2,4-dimethylcarboxanilido)-naphthalene-1′-(2-hydroxybenzene) in 95% ethanol. Add 0.5 ml of $0.08M$ sodium tetraborate solution, in order to adjust the pH to 8.95 and make up to the mark with 95% ethanol. Measure the absorbance of this solution in a 1-cm cell at a wavelength of 505 mμ against a blank. Prepare the blank by adding 10 ml of water and 0.5 ml of $0.08M$ sodium tetraborate solution to 5 ml of the reagent solution and making up to volume with 95% ethanol. Calculate the amount of magnesium with the aid of a calibration graph, prepared by carrying 10-ml aliquots of standard magnesium solutions through the last part of the procedure in which the coloured magnesium complex is formed.

RESULTS

In order to check the procedure described above, solutions of zinc sulphate of analytical grade, containing 400 mg of zinc per 25 ml, to which known amounts of magnesium had been added, were analysed. The results are listed in Table II. The amounts of magnesium are given in p.p.m. with respect to zinc.

TABLE II

Mg present p.p.m.	*Mg found* p.p.m.	Δ = *present — found* p.p.m.	*Recovery* %
198	203	— 5	102.5
198	203	— 5	102.5
396	376	+ 20	95.2
396	380	+ 16	96.0
594	579	+ 15	97.5
594	595	— 1	100.2
792	785	+ 7	99.1
792	818	— 26	103.3
990	970	+ 20	98.0
990	976	+ 14	98.6
	mean	+ 6	99.3
	st. dev.	10	2.8

Magnesium was also determined in zinc sulphate containing other impurities, *viz.* 150 p.p.m. of manganese, 100 p.p.m. of iron, 40 p.p.m. of nickel, 150 p.p.m. of aluminium, 75 p.p.m. of lead and 250 p.p.m. of calcium, all with respect to zinc. The results are given in Table III.

TABLE III

Mg present p.p.m.	*Mg found* p.p.m.	Δ = *present — found* p.p.m.	*Recovery* %
200	205	— 5	102.5
200	192	+ 8	96.0
400	385	+ 15	96.2
400	409	— 9	102.2
600	586	+ 14	97.7
600	590	+ 10	98.3
	mean	+ 6	98.8
	st. dev.	10	2.9

DISCUSSION

From Tables II and III it can be seen that the method yields precise and accurate results. The mean recovery percentages do not differ significantly from 100% and the standard deviations of the difference between ,,present" and ,,found" are satisfactory.

An advantage of the method over that using Eriochrome Black T as a reagent, is that the method is applicable to solutions containing amounts of calcium of the same order of magnitude as those of magnesium. In the Eriochrome Black T method a correction must be applied when calcium is present[12].

Finally, it should be remarked that the procedure has the additional advantage of allowing the determination of aluminium, as this has to be removed by extraction of the 8-hydroxyquinolate with chloroform, which, according to GENTRY AND SHERRINGTON[13], can be determined spectrophotometrically.

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SUMMARY

The spectrophotometric determination of magnesium in the presence of large amounts of zinc is described. Zinc as well as some other interfering metals are removed by mercury cathode electrolysis and aluminium is removed by a chloroform extraction with 8-hydroxyquinoline.

RÉSUMÉ

Une méthode spectrophotométrique est décrite pour le dosage du magnésium en présence de grandes quantités de zinc. Le zinc et quelques autres métaux interférents sont séparés par électrolyse avec une cathode de mercure; l'aluminium est éliminé par extraction au chloroforme avec le 8-hydroxyquinoline.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Methode zur Bestimmung von Magnesium neben grossen Mengen Zink beschrieben. Zink sowie einige andere störenden Metalle werden entfernt mittels Elektrolyse an einer Quecksilberkathode und Aluminium wird entfernt mittels einer Chloroformextraktion mit 8-Hydroxychinolin.

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APPLICATION DE LA DIPHÉNYL-ACROLÉINE À L'ANALYSE FONCTIONNELLE

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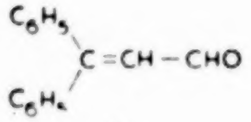
C'est souvent par le jeu de structures conjuguées que l'on interprète le mécanisme de nombreuses réactions colorées. La formation de cycles insaturés ou de structures quinoniques en sont des exemples classiques, de même que l'entrée en conjugaison de systèmes insaturés préexistants. A cet égard, la diphényl-acroléine, I, non encore utilisée en analyse, laisse prévoir, par sa structure, l'obtention facile de dérivés colorés.



$$\begin{matrix}C_6H_5 & \\ & C=CH-CHO\\ C_6H_5 & \end{matrix}$$

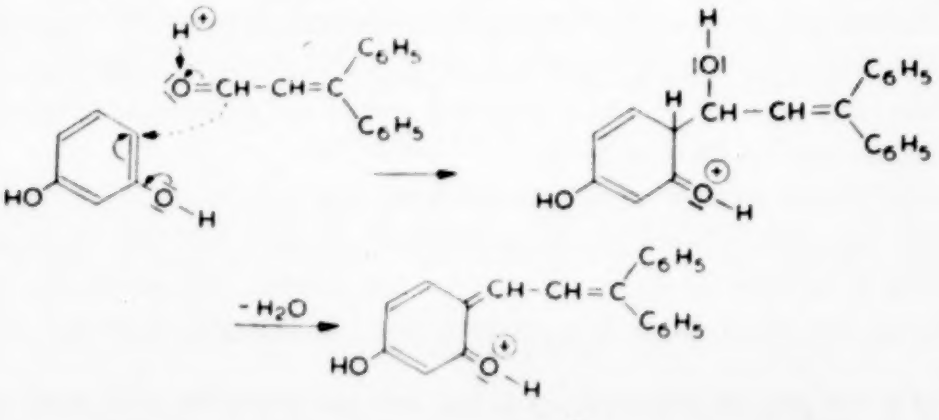
I

Nous décrivons ici sommairement plusieurs condensations intéressant l'analyse organique fonctionnelle.

(1) En milieu alcoolique fortement acide, la diphényl-acroléine développe à froid, avec les composés ayant au moins *deux hydroxyles phénoliques en méta*, une coloration rouge.

A 2 ml de solution méthanolique d'un *m*-diphénol, on ajoute 2 ml de solution à 1% de diphényl-acroléine dans le méthanol et 1 ml d'acide chlorhydrique concentré. Après 20 min à température ordinaire, le maximum d'absorption est situé à 4850 Å (résorcinol, phloroglucinol, orcinol) ou 5000 Å (naphtorésorcinol, pyrogallol).

La vitesse d'apparition de la coloration varie avec le solvant. Le méthanol permet d'obtenir une sensibilité de 1 µg, que l'on n'atteint pas en éthanol. L'addition d'eau fait disparaître la coloration. Enfin, cette réaction liée à la position *méta* des deux hydroxyles permet d'effectuer des dosages. La loi de Beer est satisfaite au maximum d'absorption pour des prises d'essai généralement comprises entre 2 et 10 µg.

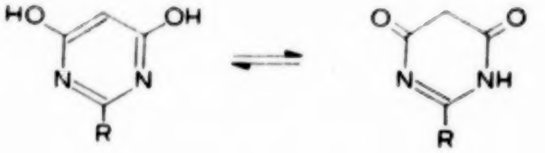


II

Le mécanisme de la réaction n'a pu, jusqu'à présent, être établi, le colorant n'ayant pas été isolé à l'état pur. Par analogie avec les autres condensations décrites ici et en raison de la sélectivité de la réaction, nous croyons cependant pouvoir suggérer une attaque électrophile du *m*-diphénol par la diphényl-acroléine qui aboutit à une structure *o*-quinonique, II.

Cette hypothèse est en accord avec le fait que l'acide résorcinol 4,6-disulfonique ne développe aucune coloration, et que cette coloration est, par contre, observée avec le *m*-diméthylamino phénol.

(2) Dans les mêmes conditions que précédemment, les *méthylènes en α du carbonyle* des cyclanones sont également réactifs. Les colorations sont jaune à jaune-vert avec les cyclopentanone et cyclohexanone. La cyclohexane 1,3-dione et son dérivé 5,5-diméthylé ou dimédone réagissent toutefois assez peu. Les 4,6-dihydroxy pyrimidines fournissent, par contre, des colorations rouges ou orangées. La sensibilité atteint le *μ*g avec la 2-éthyl-4,6-dihydroxy pyrimidine, III*, la 2-carbamylméthyl-4,6-dihydroxy pyrimidine, IV, et l'acide barbiturique, V.

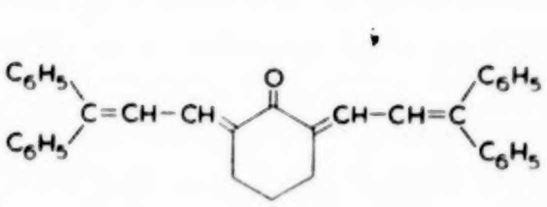


III R = C_2H_5-

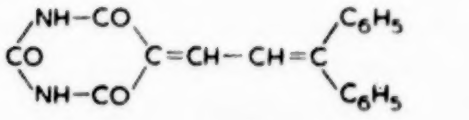
IV R = H_2N-CO-CH_2-

V R = -OH

Les dérivés formés à partir de la cyclohexanone et de l'acide barbiturique ont été isolés. Nous leur avons attribué les structures VI et VII:



VI



VII

La réaction n'est pas fournie par les méthylènes activés rencontrés en série aliphatique: malonate et cyanacétate d'éthyle, acétylacétone et acétylacétate d'éthyle. Par contre, l'indole non carbonylé, mais existant sous une forme méthylénique en *β* de l'azote développe une coloration rouge.

(3) Les *amines aromatiques* primaires offrent, par action de la diphényl-acroléine en milieu acide, des colorations jaune orangé qui ne sont pas fournies par les amines aliphatiques ou aromatiques substituées. Au maximum d'absorption, vers 4000 Å, la loi de Beer est satisfaite pour des prises d'essai inférieures à 20 *μ*g.

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* Ce composé a été préparé selon HULL[1] et BROWN[2] par action du propionate de méthyle sur le diamide malonique.

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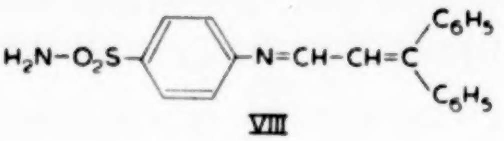
Il s'agit là d'une formation de bases de Schiff. Nous avons isolé une de ces bases, VIII, à partir du *p*-amino benzènesulfonamide, en raison de la faible solubilité de son chlorhydrate.



VIII

PARTIE EXPÉRIMENTALE

(avec Mlle G. CLÉMENT)

2,6-Bis-diphénylallylidène cyclohexanone, VI.

On ajoute 1 ml d'acide chlorhydrique concentré à 0.5 g de cyclohexanone et 1.0 g de diphényl-acroléine en solution dans 7 ml de méthanol puis abandonne pendant 3 jours à température ordinaire. Le cristallisat jaune-vert obtenu est isolé puis lavé au méthanol et à l'éther (0.7 g). F.inst.: 207°.

Analyse: $C_{36}H_{30}O = 478.6$

Calculé:	C	90.3	H	6.3	O	3.3
Trouvé:		90.1		6.5		3.8

Diphénylallylidène malonylurée, VII.

Dans 35 ml de méthanol, on dissout 0.5 g d'acide barbiturique et 0.82 g de diphényl-acroléine, puis ajoute 5 ml d'acide chlorhydrique concentré. Après amorçage et quelques heures de repos, on essore, lave au méthanol et à l'éther (1.0 g). F.inst.: 330° (déc.).

Analyse: $C_{19}H_{14}O_3N_2 = 318.3$

Calculé:	C	71.7	H	4.4	O	15.1	N	8.8
Trouvé:		71.7		4.4		15.3		8.8

p-(Diphénylallylidène-amino) benzènesulfonamide, VIII.

À la solution de 0.5 g de *p*-amino benzènesulfonamide et 0.6 g de diphényl-acroléine dans 15 ml de méthanol, on ajoute 2 ml d'acide chlorhydrique concentré. Après 2 heures au repos, on essore, lave au méthanol et à l'éther (0.9 g). F.inst.: 230–235°.

Analyse: $C_{21}H_{18}O_2N_2S \cdot HCl = 398.9$

Calculé:	C	63.2	H	4.8	O	8.0	S	8.0
Trouvé:		63.3		4.7		7.9		7.7

RÉSUMÉ

En milieu alcoolique fortement acide, la diphényl-acroléine développe, à froid, avec les *m*-diphénols une coloration rouge. Cette réaction, qui permet d'effectuer des dosages, offre une sensibilité de 1 *μg*. Dans les mêmes conditions, on obtient des colorations jaunes avec les méthylènes situés en *α* d'un carbonyle ou avec les groupes aminés aromatiques primaires. Plusieurs produits de condensation ont pu être isolés.

SUMMARY

In highly acid alcoholic medium, diphenyl-acrolein develops a red colour with *m*-diphenols, in the cold. This reaction, which makes it possible to carry out determinations, has a sensitivity of one *μg*. Under the same conditions, yellow colouring is obtained with methylenes in the *α* position of a carboxyl or with primary aromatic amino groups. Various condensation products have been isolated.

ZUSAMMENFASSUNG

Diphenyl-acrolein gibt mit *m*-Diphenolen in stark saurer, alkoholischen Lösung in der Kälte eine rote Färbung. Empfindlichkeit der Reaktion: 1 *μg*. Methylengruppen, in *α* Stellung zu einer Carbonylgruppe oder primäre aromatische Aminogruppen geben unter den gleichen Bedingungen eine gelbe Färbung. Einige der Kondensationsprodukte konnten isoliert werden.

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Reçu le 23 mai 1958

POLAROGRAPHIC REDUCTION OF HEXAVALENT URANIUM IN SODIUM TRIPOLYPHOSPHATE

II. ESTIMATION OF URANIUM

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An acid supporting electrolyte is generally used for the polarographic estimation of uranium. The reduction of UO_2^{+2} can be carried to the penta- or even tetravalent stage by controlling the acidity[1,2,3]. The $E^1/_2$ (around -0.3 V *vs.* S.C.E.) for the reduction of the uranyl ion is inconveniently close to the reduction potentials of several common ions. STRUBL[4] avoided the interference from ferric iron by using hydroxylamine hydrochloride. It has been reported that a 50% solution of ammonium citrate[5] adjusted to pH 4–5 eliminates the interference caused by small amounts of copper and lead. Reduction in ascorbic acid medium at pH 3.5–4, recommended by ŠUŠIĆ *et al.*[6], also offers certain advantages.

Alkaline supporting electrolytes have not been much used in the polarographic estimation of uranium, though there is the probable advantage that many elements such as tungsten, molybdenum, titanium, tin, antimony and niobium might cease to interfere. Alkaline solutions of uranyl complexes undergo a one-electron reduction with an $E^1/_2$ around -0.7 to -1.1 V. The uranium waves in alkali carbonate[7] and in alkali citrate/tartrate[8] are regarded unsuitable for analytical work, but PŘIBIL AND BLAŽEK[9] have used a combination of EDTA and sodium carbonate for uranium estimation with some success. The present paper reports a method for the estimation of uranium based on the reduction of the uranyl tripolyphosphate complex in an alkaline medium.

EXPERIMENTAL

The experimental set-up was substantially the same as described in a previous communication[10]. Uranyl nitrate was used as the standard.

Uranyl concentration vs. diffusion current

All polarograms were taken in presence of 0.005% camphor in the solution, which was observed to improve the shape of the reduction wave considerably, without materially affecting the diffusion current. The height of the wave was corrected for the residual current by graphical extrapolation. The proportionality between *id* and *c* is shown in Table I.

Interferences

In addition to those anionic radicals which are polarographically inactive in the alkaline medium (WO_4^{-2}, MoO_4^{-2} etc.), several cations, *e.g.*, Cr^{+3}, Co^{+2}, Ni^{+2}, Mn^{+2}

TABLE I

id VERSUS URANYL ION CONCENTRATION

Electrolyte composition: uranyl nitrate, 1 *M* KNO_3, 0.1 *M* $Na_5P_3O_{10}$, 0.005% camphor (m = 1.68 mg/sec, t = 4.204 sec/drop)

Uranyl ion (mM)	*id (μa × 100)*	*id/c*
0.2	56	280
0.5	142	284
1.0	280	280
2.0	556	278
3.0	830	277
5.0	1370	274

and Zn^{+2} were found not to interfere. By complexation with tripolyphosphate, the reduction potentials of these cations became too negative to give cathodic steps in the accessible potential range. Among ions which undergo reduction in an alkaline tripolyphosphate medium, Pb^{+2} and Bi^{+3} have $E^1/_2$ values that are fairly well in advance of the uranyl wave (Pb^{+2} —0.65, Bi^{+3} —0.63, UO_2^{+2} —1.05 V)[10], and do not interfere in low concentrations. Uranium estimations in a few synthetic mixtures containing these non-interfering ions are reported in Table II. The method of standard addition[11] was used throughout to compute uranium concentrations from the polarograms, because the *id* for this reduction varies somewhat with pH, total ionic strength type and concentration of maximum suppressor used, etc.[10]

TABLE II

ESTIMATION OF URANIUM IN SYNTHETIC MIXTURE

Addition to electrolyte (mM)	*UO_2^{+2} taken (mM)*	*UO_2^{+2} found (mM)*
MoO_4^{-2} 10 WO_4^{-2} 10 Ti^{+4} 5	0.50	0.52
ditto	1.00	1.06
ditto	2.00	2.02
Cr^{+3} 10 Ni^{+2} 10 Zn^{+2} 10 Mn^{+2} 10 Co^{+2} 10	0.50	0.54
ditto	1.00	1.03
ditto	2.00	1.96
Pb^{+2} 2 Bi^{+3} 2	1.00	1.04

Separation of uranium with orthophosphate

While the estimation of uranium is thus possible in the presence of many impurities, a method of general applicability will almost always involve a preliminary separation of the uranium from some interfering elements. MILNER AND EDWARDS[12] have recently reported that uranium can be separated from a host of elements by precipitating as uranyl ammonium phosphate in presence of EDTA. A few, *e.g.*, tin, molybdenum, tungsten, titanium and beryllium co-precipitate with uranium since they do not form sufficiently stable complexes with EDTA. But, fortunately, their removal is not essential for the present method of estimating uranium.

The following EDTA–phosphate procedure was, therefore, adopted as the general method for estimating uranium in complex mixtures:

The acidic solution containing uranium is rendered faintly alkaline with ammonia, 3 g disodium salt of EDTA (Merck's Reagent) are added, and the solution boiled for 5 min to facilitate complexation. The solution (not exceeding 200 ml in volume) is buffered with an equimolar mixture of ammonium acetate–acetic acid, about 10 mg beryllium (as chloride) and 2 g solid diammonium phosphate are added, and the solution is boiled for 10 min. After further digesting on the water-bath for 30 min, the precipitate is filtered, washed with a solution containing 2% ammonium nitrate and 1% disodium salt of EDTA, and dissolved in dilute nitric acid (1:4).

TABLE III

ESTIMATION OF URANIUM IN SYNTHETIC MIXTURES

(Before polarographing, the uranium was separated by the EDTA–phosphate procedure).

Synthetic sample[a] *composition (mg)*	*Uranium taken (mg)*	*Uranium found (mg)*
Fe^{+3} 50 Cu^{+2} 50 V^{+5} 50	2.38	2.46
ditto	4.76	4.83
ditto	7.14	7.05
Pb^{+2} 70 Bi^{+3} 70 Cr^{+3} 80	2.38	2.32
ditto	4.76	4.84
ditto	7.14	7.00
Ti^{+4} 20 WO$_4^{-2}$ 50 MoO$_4^{-2}$ 50	2.38	2.47
ditto	4.76	4.86

[a] All the samples contained 10 mg Be^{+2} as the chloride.

The acidic solution is neutralised with ammonia to pH 3–5 with the help of indicator paper, 2 g anhydrous sodium tripolyphosphate and 1 ml of 0.25% camphor solution are added, mixed and the solution is made up to 50 ml. (While making a stock solution of the sparingly soluble camphor, addition of a little alcohol helps to bring about easy dissolution). Aliquots are then transferred to the electrolytic cell and polarographed.

Table III shows some of the results obtained by the above procedure. Incomplete recovery of uranium was indicated in the absence of beryllium coprecipitant, particularly when the uranium taken was below a few mg. Below 1 mg level, uranium recoveries were erratic. All the polarograms were free from any steps other than the one for uranyl ion. The EDTA–phosphate procedure, therefore, gives a complete separation from interfering elements such as cadmium, copper, bismuth, lead, vanadium and ferric iron.

Estimation of uranium in minerals

A few samples of uraniferous ores were analysed for their uranium contents by the new method. Two samples of tantalo-niobate taken for analysis contained as major constituents Nb, Ta, Ti, Fe, Mn and Ca. The only other sample analysed was a Travancore monazite.

Procedure for tantalo-niobate

The sample (2 g, ground to 100 mesh) is weighed into a platinum basin, decomposed with a mixture of nitric and hydrofluoric acids and taken to fumes with sulphuric acid. The fumed mass is transferred with a jet of water to a 500-ml beaker, almost neutralised with ammonia and then re-acidified with 2 ml of nitric acid. On diluting to about 300 ml and boiling, practically all the tantalum and niobium along with most of the titanium precipitate out leaving the uranium in solution. After filtration, the precipitate is washed with 1:5 nitric acid. The filtrate is boiled down to about 200 ml and subjected to the EDTA–phosphate procedure. The analysis is completed polarographically by the method of standard addition as already described.

Procedure for monazite

The sample (2 g, ground to 100 mesh) is weighed into 250-ml pyrex beaker and

TABLE IV

ANALYSIS OF URANIFEROUS ORES

Sample	*Uranium content*	
	Procedure under test (%)	*Alternative procedure* (%)
Tantalo-niobate (I)	0.36	0.37
Tantalo-niobate (II)	0.52	0.54
Travancore monazite	0.32	0.34

decomposed with concentrated sulphuric acid. The pasty mass is diluted and boiled with 200 ml of 15% sodium carbonate. It is filtered and the residue boiled with sodium carbonate once again to ensure quantitative extraction of uranium. The combined filtrates are neutralised with dilute nitric acid, boiled down to about 200 ml and subjected to the EDTA-phosphate procedure. The polarographic analysis is then completed as before.

Results of analyses of the minerals are shown in Table IV. The alternative procedure indicated in the Table refers to the conventional colorimetric method with peroxide after extracting the uranium with ether from an aqueous nitrate solution.

For accurate work with complex materials, the sample taken for analysis should contain not less than 2-3 mg of uranium. When interfering elements, *viz.* copper, cadmium, iron, vanadium and large amounts of lead and bismuth are absent, and a preliminary separation of the uranium by the EDTA-phosphate procedure is not indicated, even fractions of a mg of uranium can be estimated, since solutions as dilute as $10^{-4}M$ with respect to uranyl give measurable diffusion currents in an alkaline tripolyphosphate medium.

SUMMARY

A polarographic method of estimating of uranium, based on the reduction of its tripolyphosphate complex at the dropping mercury electrode, has been developed and applied to uraniferous tantaloniobates and monazite. In the presence of elements such as copper, iron and vanadium which interfere with the cathodic step of the uranyl complex, a preliminary separation as uranyl ammonium phosphate in presence of EDTA is necessary.

RÉSUMÉ

Une méthode polarographique est proposée pour le dosage de l'uranium; elle peut être appliquée à l'analyse de tantalo-niobates uranifères et de la monazite.

ZUSAMMENFASSUNG

Es wird eine polarographische Methode zur Bestimmung des Urans beschrieben. Sie lässt sich für die Analyse uran-haltiger Tantal-niobate und Monazit anwenden.

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A SIMPLE APPARATUS FOR THE DETERMINATION OF MERCURY BY AMALGAMATION WITH GOLD

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INTRODUCTION

Difficulty had been experienced in one of our laboratories in obtaining consistent results for the estimation of mercury in charcoal which had been activated by treatment with mercuric chloride. The method used was essentially that of ESCHKA[1] which involves heating the sample with iron powder and quicklime[2] (or zinc oxide) in a silica crucible and amalgamating the mercury, liberated as vapour, on a weighed gold lid. The gold lid is placed on top of the crucible and is cooled by water. The main disadvantage of this procedure is the possible leakage of mercury vapour between the gold lid and the top of the crucible. It was considered, therefore, that the design of an apparatus which would eliminate this difficulty would result in more consistent and accurate results.

EXPERIMENTAL

The apparatus used is shown in Fig. 1. It consists of a straight silica column about 10 cm long and 0.6 cm in diameter loosely packed with gold foil. The bottom of the column fits into a small silica flask containing a mixture of the sample and iron powder which is covered with a thin layer of zinc oxide. On heating, the mercuric chloride is reduced to mercury and the mercury content of the sample is calculated from the increase in weight of the column containing the gold foil.

The apparatus was first tested on AnalaR mercuric chloride, and then on mixtures of charcoal and known amounts of mercuric chloride. The effect of small amounts of impurities was also tested.

Analyses were also carried out by different operators on actual samples of charcoal which had been activated by treatment with mercuric chloride. Three of the operators were applying the method for the first time. The results obtained are shown in Tables I and II.

It is evident, therefore, that the precision is good and that no operator bias is likely to arise in the application of the method. The procedure cannot be applied, of course, in the presence of metals which are volatile at the temperature of the determination and which alloy with gold.

Apparatus

As in Fig. 1.

Cut the gold foil (about 0.0025 cm thick) into strips about 0.3 cm × 2.5 cm. Bend two of these strips at right angles at both ends and place them diagonally across each other inside the silica column. Crumple other strips lightly with the fingers and place them in the column. The column should be filled to a height of about 5–6 cm; this usually requires about 5–6 g of gold foil.

TABLE I

ANALYSIS OF MIXTURES CONTAINING KNOWN AMOUNTS OF MERCURY

Sample	*Mean % Hg*[a] *recovered*	*No. of determinations*	*Estimated standard deviation*	*Impurities added*
Pure $HgCl_2$	98.9	10	1.20	Nil
Mixtures of charcoal and $HgCl_2$	98.9	12	1.34	
	99.8	4	0.62	1% Na_2S
	98.8	6	0.73	0.1% As_2O_3 0.2% KH_2PO_4 0.15% Na_2SO_3

[a] The amount of mercuric chloride per determination ranged from 50–100 mg.

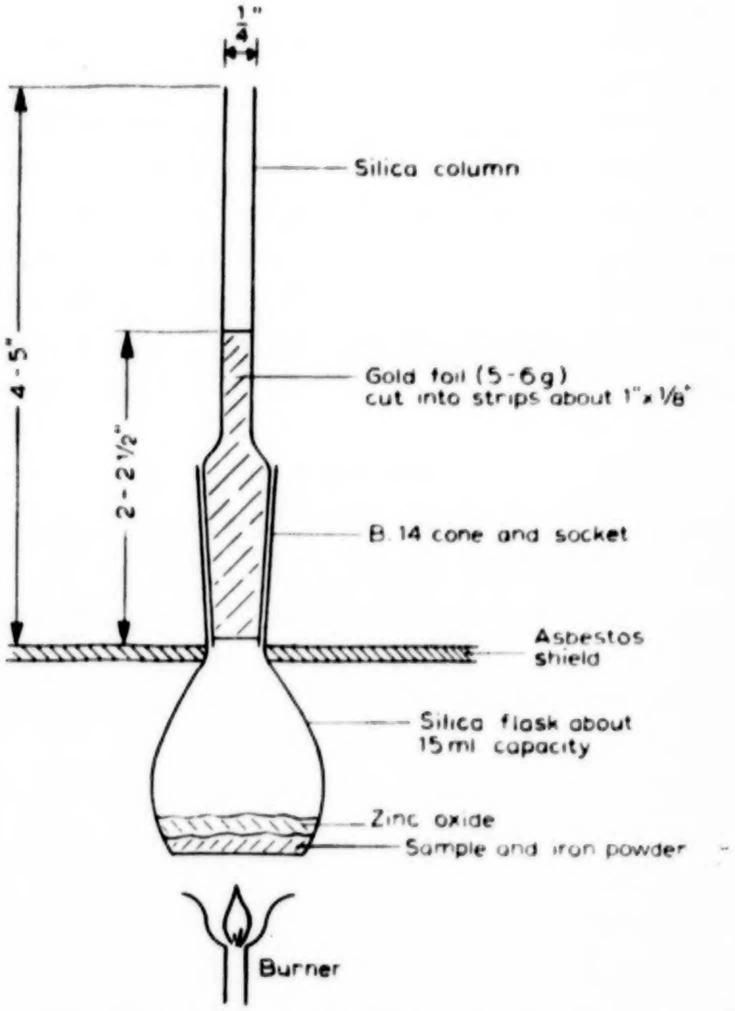
1/4"
Silica column
4-5"
2-2½"
Gold foil (5-6g) cut into strips about 1"×1/8"
B.14 cone and socket
Asbestos shield
Silica flask about 15ml capacity
Zinc oxide
Sample and iron powder
Burner

Fig. 1. Apparatus for the determination of mercury.

TABLE II

ANALYSES CARRIED OUT BY DIFFERENT OPERATORS ON ACTUAL SAMPLES

Operator	*Mean % mercury (as Hg)*	*No. of determinations*	*Estimated standard deviation*
1	3.00	10	0.08
2	3.00	5	0.04
3	2.97	6	0.05
4	2.98	4	0.05

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Reagents

Iron powder: A.R. grade; to pass 100-mesh sieve; Zinc oxide: A.R. grade; Acetone.

Procedure

Weigh accurately about 1 g of the sample into the silica flask. The sample should contain not more than 70 mg of mercury. Add about 1 g of fine iron powder and mix by gently swirling the flask. Cover the mixture with about 0.3-cm layer of zinc oxide and insert the column, which has been previously rinsed with acetone, dried and weighed, into the silica flask. Place a shield of asbestos, with a hole in the middle, round the neck of the silica flask and heat the bottom of the flask, first with a low flame for 10 minutes and then at a dull red heat for 20 minutes. Allow the apparatus to cool, remove the column, rinse it with acetone, dry and weigh. After each determination, the column can be regenerated by heating it in a bunsen flame and passing air through it to remove the mercury.

ACKNOWLEDGEMENTS

Thanks are due to Mr. V. R. CONRADI who carried out most of the experimental work and to African Explosives and Chemical Industries, Limited, for permission to publish this paper.

SUMMARY

The method of ESCHKA for the determination of mercury by amalgamating with gold has been modified by using a simple apparatus which eliminates errors caused by loss of mercury vapour. The method does not require a skilled operator and it is suitable for routine analysis. For a sample containing 3% mercury, the estimated standard deviation is 0.06.

RÉSUMÉ

L'auteur propose une modification de la méthode d'ESCHKA pour le dosage du mercure par amalgamation de l'or, en utilisant un appareil simple qui permet d'éliminer des erreurs par perte de vapeur de mercure.

ZUSAMMENFASSUNG

Es wird eine Modifikation der Methode nach ESCHKA zur Bestimmung von Quecksilber als Gold-Amalgam beschrieben, wobei ein einfacher Apparat verwendet wird, der Fehler durch Verlust von Quecksilberdampf verhindert.

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Short Communications

The use of 4-amino-4′-chlorodiphenyl as reagent for the determination of sulphate

The original estimation of the solubility of the dried amine sulphate led us to believe that 4-amino-4′-chlorodiphenyl sulphate was only slightly more soluble than barium sulphate[1], but after the reagent had been in routine use for some time it became apparent that the freshly precipitated sulphate was considerably more soluble[2].

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Redetermination of the solubility of samples of the *freshly* precipitated salt were made by two methods. The evaporation to dryness and constant weight of 100 ml of a saturated solution of the amine sulphate gave a residue of 8 mg, corresponding to an apparent solubility of 80 mg. Titration of 20-ml aliquots of the same solution with 0.025*N*-sodium hydroxide gave a mean value for the acidity as equal to 0.614 ml of *N*-sodium hydroxide per l. Taking the equivalent weight of the amine sulphate as 254, the solubility becomes 155 mg/l.

BENGTSSON[3] has recently advanced an interesting explanation for the contradictory values for the solubility, based on the equilibrium conditions for the system amine sulphate–water. Because of the sparing solubility of the amine itself in water, its solubility is exceeded before final equilibrium is reached, and thus it precipitates. Determination of the solubility of a saturated solution of the amine salt then gives erroneous results when the solution is evaporated to dryness and the residue is weighed. This possible source of error had been overlooked because earlier determinations on benzidine derivatives involved amines which were all more soluble in water than their corresponding sulphates[4]. This is an extremely important point which has never been adequately appreciated.

The fact that the solubility of the amine sulphate is higher than was originally believed does not affect the use of the reagent under the recommended conditions[2]. Sensitivity data show that a much smaller amount of sulphate ion is detectable in solution in the presence of excess reagent than is present in a saturated solution of the amine sulphate (prepared by shaking the amine sulphate with water for three days). The reagent can readily detect 10 μg of sulphate ion (formed as a precipitate) in a total volume of 50 ml which corresponds to a dilution of 1 : 5·10^6. The amount of sulphate ion present in 1 l of saturated solution of the amine sulphate is approximately 30 mg. From the sensitivity data, 1 ml of saturated amine sulphate should give a definite turbidity with the reagent solution and this can readily be verified. But 1 ml of the amine sulphate solution contains approximately 30 μg of SO_4^{-2}, therefore the amount of sulphate ion remaining in solution must be considerably less than this for an observable precipitate to be obtained.

BENGTSSON concluded on purely theoretical grounds that the reagent is unsuitable for sulphate determinations on the micro-scale because of the solubility of the amine sulphate. He has found by spectrophotometric methods (*cf.* JONES AND LETHAM[5]) that 1 l of the saturated solution of 4-amino-4′-chlorodiphenyl sulphate contains 31.2 mg of sulphate ion and 40.8 mg of amine, which corresponds to a deficiency of amine of 91.8 mg. BENGTSSON's values for the solubility are in close agreement with our results, namely, 80 mg/l for the apparent solubility (BENGTSSON, 72 mg/l and 155 mg/l for the theoretical solubility (BENGTSSON, 164 mg/l).

We can only conclude from BENGTSSON's remarks that he has not appreciated the remarkable sensitivity of the reagent towards sulphate ions. He considers that solubility is the prime factor which can influence the suitability of an analytical reagent, whereas we accept FEIGL's view that the sensitivity of the reagent is the more important criterion.

References p. 199

BENGTSSON's suggestion for improving the use of the reagent by halving the amount of free hydrochloric acid in the reagent solution thus, in his words, 'favouring the completeness of the precipitation by a factor of two or three owing to the increased pH and lower ionic strength of the solution' offers no advantage over the original reagent, and in fact, has the disadvantage of crystallising out the amine hydrochloride more readily on standing, thus decreasing the already limited strength of the reagent solution.

BENGTSSON states that 'since the solubility product of the amine sulphate is $0.8 \cdot 10^{-11}$, the amount of sulphate left in solution is *calculated* to be 30 μg. But this cannot be reconciled with the fact that the reagent will under quite standard conditions give an observable precipitate not only with 31 μg of sulphate ion in 1 ml of a saturated solution of the amine sulphate (BENGTSSON's figure), but with as little as 10 μg.

4-Amino-4'-chlorodiphenyl is the most sensitive reagent known for the precipitation of the sulphate ion. This can readily be shown by adding to three 50-ml Nessler glasses 10 ml of a solution containing 5 μg/ml of SO_4^{-2} and diluting each glass to the mark with equivalent solutions of barium chloride, benzidine hydrochloride and 4-amino-4'-chlorodiphenyl hydrochloride respectively. Only with the last reagent does a well-defined turbidity develop which is still apparent when the test solution of sulphate is diluted 5 times. Hence precipitation of sulphate is even more complete than with barium.

Provided that the proper care (which we have always stressed) is taken in the washing procedure, the reagent is capable of giving very accurate results over a wide range of sulphate concentrations. BENGTSSON's arguments against the suitability of 4-amino-4'-chlorodiphenyl as an analytical reagent could be applied equally well to a great number of analytical precipitants, for example, the double uranyl acetate reagents for sodium. Nevertheless, such reagents are extensively used in quantitative analytical procedures with satisfactory results.

During the years following the proposal of the present reagent, considerable interest has been aroused by its many possible applications. Successful procedures have been adopted in a number of laboratories and sufficient published data exist for the reagent to be the subject of a forthcoming review.

The University, Edgbaston, Birmingham (Great Britain)

R. BELCHER
W. I. STEPHEN

[1] R. BELCHER, A.J. NUTTEN AND W.I.STEPHEN, *J. Chem. Soc.*, (1953) 1334.
[2] R. BELCHER, A.J. NUTTEN, E. PARRY AND W.I. STEPHEN, *Analyst*, 81 (1956) 4.
[3] T.A. BENGTSSON, *Anal. Chim. Acta*, 18 (1958) 353.
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[5] A.S. JONES AND D.S. LETHAM, *Analyst*, 81 (1956) 15.

Received October 17th, 1958

Solubility products of gadolinium bicarbonate

Although this compound has not been previously reported, the bicarbonate of calcium and other alkaline earths are well known. SÖRENSEN[1], in reporting on the Winkler method[2] for caustic alkalies, states that in the addition of barium chloride to a carbonate solution appreciable bicarbonate is coprecipitated. In this study a preweighed amount of gadolinium oxide was dissolved in perchloric acid. This solution was then titrated in increments with standard sodium carbonate and the pH was observed by means of a model #2 Beckman pH meter. A curve of the type shown in Fig. 1 was obtained by plotting pH as a function of solution added. The portion A′ —C represents the precipitation of the bicarbonate. The portion A —A′/2) represents the titration of excess perchloric acid. The pH at point B(B = C —A′/2) was used to obtain the hydrogen ion concentration resultant from the bicarbonate equilibrium. From the equivalents of carbonate consumed in the portion A′ —C it was found that the ratio of gadolinium to carbonate was 1:3, which has a variance of 0.12. The precipitate was dried over dehydrate and when analyzed gave 55.2% ignited oxide (R_2O_3). This compared with 50.6% for the bicarbonate compound. Oven drying caused thermal decomposition and conversion to the carbonate.

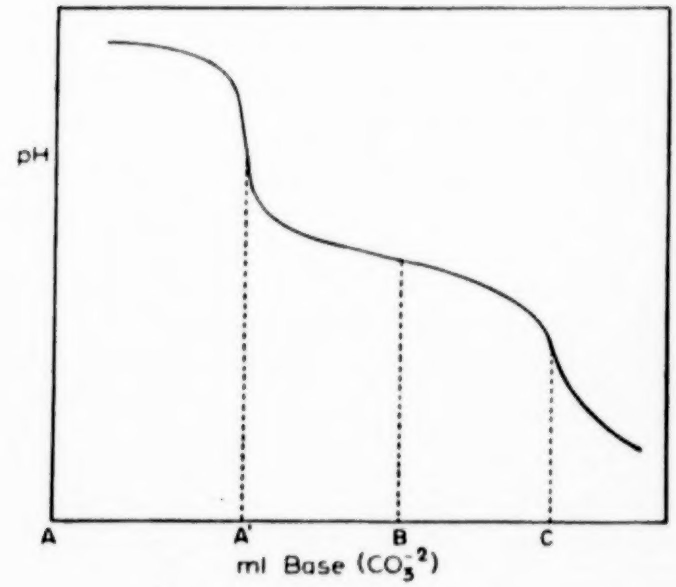

Fig. 1. Typical titration curve.

The solubility product was evaluated from the known hydrogen ion concentration at point B, and the fact that at B the concentration of the gadolinium ion is about one-half of that at A′. The hydrogen ion concentration coupled with the carbonate equilibrium ($K = 4.5 \cdot 10^{-11}$) gave the bicarbonate concentration[3]. Table I gives the pertinent data for the observed solubilities of this material. The normally expected result is rising solubility with increasing temperature.

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TABLE I

SOLUBILITY PRODUCT DATA FOR GADOLINIUM BICARBONATE

Temperature	*pH at B*	$Gd(HCO_3)_3$
10	5.26	$9.7 \cdot 10^{-3}$
20	5.24	$13 \cdot 10^{-3}$
30	5.14	$20 \cdot 10^{-3}$
40	4.95	$340 \cdot 10^{-3}$

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C. C. MELOCHE**

[1] S. P. L. SÖRENSEN AND A. C. ANDERSON, *Z. anal. Chem.*, 45 (1906) 220.
[2] I. M. KOLTHOFF AND V. A. STENGER, *Volumetric Analysis*, Vol. 2, Interscience, New York, 1947, p. 10.
[3] I. M. KOLTHOFF AND V. A. STENGER, *Volumetric Analysis*, Vol. 1, Interscience, New York, 1947, p. 151.

Received August 30th, 1958

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REVUE DE LIVRE

Manual of Analytical Methods Recommended for Sampling & Analysis of Atmospheric Contaminants, publié par le Committee on Recommended Analytical Methods – American Conference of Governmental Industrial Hygienists, Cincinnati 2, Ohio, 1958, Prix $ 5.00.

L'ouvrage que nous avons en mains est un recueil de méthodes concernant le dosage de divers poisons dans l'atmosphère. Il est le résultat d'un travail collectif et critique, travail dû à un Comité désigné par l',,American Conference of Governmental Industrial Hygienists''.

Présenté sous forme de classeur avec des feuilles interchangeables, il permet au lecteur d'y joindre les méthodes que le Comité fera paraître ultérieurement et dont les neuf premières sont comprises dans le prix indiqué plus haut.

Bien que soumises à un contrôle sévère, les marches à suivre proposées souffrent d'un certain manque de détails, ce qui pourrait quelque peu étonner un lecteur habitué aux publications américaines de ce genre (celles de l'A.S.T.M., par exemple). De même, à notre avis, les références bibliographiques pourraient être plus riches, spécialement dans le cas du plomb. (Comparer au rapport de l'American Public Health Association Inc.: *Methods for Determining in Air and in Biologic Materials*).

En dépit de ces remarques, nous nous faisons un plaisir de reconnaître que les exposés sont très clairs et les modes opératoires proposés, en général, suffisamment simples pour qu'ils puissent être appliqués dans un laboratoire ordinaire.

Les rapports parus jusqu'à présent traitent successivement: l'arsenic, les hydrocarbures chlorés, le formaldéhyde, l'hydrogène sulfuré, le plomb, le manganèse, le mercure, les oxydes de l'azote, le parathion et l'anhydride sulfureux. Ils sont classés par ordre alphabétique, la pagination étant propre pour chaque élément.

En terminant, nous tenons à recommander cet ouvrage, tout particulièrement aux analystes de l'industrie chimique, persuadés qu'ils y puiseront des méthodes fort utiles pour le contrôle de l'air dans leurs établissements.

I. KAPÉTANIDIS (Genève)

BUCHBESPRECHUNG

GMELINS *Handbuch der anorganischen Chemie*, 8. Auflage, Verlag Chemie, GmbH, Weinheim, 1958.

Fortlaufend erscheinen die neuen Bände der achten Auflage des obgenannten Werkes. Mit diesen Neuerscheinungen behauptet das Werk seinen hervorragenden Platz im Schrifttum der Chemie, baut diesen sogar weiter aus. Soeben sind vier neue Bände dieses umfassendsten Werkes der anorganischen Chemie erschienen:

Sauerstoff, System-Nummer 3 (Lieferung 3), 518 Seiten (Elementarer Sauerstoff) Kart. DM 283.–.

Das Buch behandelt auf den ersten 17 Seiten die Herstellung des Sauerstoffes im Laboratorium und in der Technik. Ein spezieller Abschnitt befasst sich mit der Anreicherung und Trennung der Sauerstoffisotopen. Der grösste Teil des Bandes behandelt die physikalischen Eigenschaften des Elementes, in erster Stelle die atomaren und molekularen Grössen. Eingehend werden die Löslichkeit, die Allotropien, sowie die optischen Eigenschaften des Sauerstoffes behandelt. Abschliessend finden wir auf 196 Seiten eingehende Ausführungen über die Eigenschaften der Sauerstoff – Wasserstoff Gemische und Luft – Wasserstoff Gemische. Explosionsfähige Gemische, Schwellentemperaturen, Explosionskatalysatoren sind im letzten Abschnitt ausführlich besprochen.

Zirconium, System-Nummer 42, 448 Seiten, Kart. DM 266.–.

Mit der Entwicklung der Technik kommen immer mehr Elemente zur Geltung, die bis anhin eine untergeordnete Stellung einnahmen. Eines von diesen Elementen ist das Zirkon. Seinem neuen Rang ist im vorliegenden Bande gebührend Rechnung getragen.

Ein kurzer geschichtlicher Überblick ist gefolgt von den Abschnitten: Vorkommen, und Gewinnung von Zirkoniumverbindungen aus Erzen. Dieses letztere Kapitel behandelt ausführlich die Aufbereitung der Erze, der bei der Gewinnung und Trennung des Zirkons eine ganz besondere Bedeutung zukommt. Die folgenden 112 Seiten sind dem Elemente Zirkonium gewidmet. Seine Herstellung im Laboratorium und in der Technik, die physikalischen Eigenschaften des Metalles, das chemische und elektrochemische Verhalten und die Legierungen sind mit sehr viel Fachkenntnis und Ausführlichkeit behandelt. Dabei werden auch die Verwendungsmöglichkeiten des Metalles und seiner Eigenschaften als Werkstoff besprochen. Der letzte, grösste Abschnitt befasst sich mit den Verbindungen des Elementes wobei die technisch wichtigen Körper eingehend besonders besprochen werden.

Hafnium, System-Nummer 43, 23 Seiten, Kart. DM 22.– (Ergänzungsband).

Das Werk umfasst die Forschungsergebnisse der Jahre 1940 bis 1949. Die Geochemie des Elementes zeigt naturgemäss eine sehr grosse Verbundenheit mit dem Zirkon. Besondere Sorgfalt und Ausführlichkeit sind den Abschnitten über die analytische und technische Trennung des Elementes von Zirkon gewidmet. Die Kapitel über die Verwendung und den Eigenschaften des Metalles und die Besprechung seiner Verbindungen beschliessen das Werk.

Germanium, System-Nummer 45, 576 Seiten, Kart. DM 332.– (Ergänzungsband).

Das Werk umfasst die Jahre 1931 bis 1953/4. In dieser Zeitspanne hat das Element Germanium eine technische Wichtigkeit erlangt, die mit seiner Bedeutung zur Zeit des Erscheinens des ersten Bandes nicht verglichen werden kann. Der Umfang des Bandes hat sich demgemäss auch vervielfacht. Die ersten 27 Seiten behandeln das Vorkommen und die Geochemie des Elementes. Das folgende Kapitel ist der Gewinnung der Germaniumverbindungen aus den Erzen gewidmet. Besondere Aufmerksamkeit erhielt dabei die Herstellung reinstes Germaniums. Die physikalischen Eigenschaften, in erster Stelle die so wichtige Elektronenkonfiguration des Atoms, sind mit der charakteristischen Sorgfalt des Handbuches beschrieben. Dieser Abschnitt, der über 400 Seiten des Bandes einnimmt, ist weitaus der wichtigste Teil. Die elektrischen und lichtelektrischen Eigenschaften sind im Inhaltsverzeichnis separat gehalten was ihre Wichtigkeit wohl unterstreicht, jedoch beim ersten Durchblättern des Buches etwas irreführend sein kann.

Die Chemie des Germaniums, seine analytischen Nachweis- und Bestimmungsmethoden sind ebenfalls ausführlich behandelt. Die Legierungen und Verbindungen des Elementes–dessen besonderer Übergangscharakter auch diesem Abschnitt einen besonderen Ton verleiht, wobei es nicht zu vergessen ist, dass Germanium zu der Kohlenstoffe-Gruppe gehört–beschliessen das Werk.

H. KELLER (Genf)

SOME RECENTLY PUBLISHED BOOKS

E. Broda, *Radioaktive Isotope in der Biochemie*, Bd III, Verlag Franz Deuticke, Wien, 1958, viii + 326 S., in Ganzleinen, öst. S. 294.—, DM 49.—

M. Hudlický, *Chemie organických sloučenin fluoru, Chemie der organischen Fluorverbindungen*, Verlag der Tschechoslowakischen Akademie der Wissenschaften, Praha, 1958, 360 S., Kcs 38.50

B. Jirgensons, *Organic Colloids*, Elsevier Publishing Company, Amsterdam, 1958, xiv + 625 pp., £ 4.5.—

F. Klages, *Lehrbuch d. organischen Chemie*, Bd III, Walter De Gruyter und Co, Berlin, 1958, xix + 766 S., geb. DM 98.—, bei Einzelbezug DM 104.—

J. Maurin, *Les piles atomiques à neutrons lents*, Dunod, Paris, 1958, xii + 197 pp., relié toile souple, 980 Frs.

S. S. Penner, *Chemistry Problems in Jet Propulsion*, Pergamon Press Ltd, London, 1957, xiv + 394 pp., 90 s. net

E. H. Rodd, *Chemistry of Carbon Compounds*, Vol. IV A, Elsevier Publishing Company, Amsterdam, 1958, xxvi + 808 pp., £ 7.7.—

K. Sagel, *Tabellen zur Röntgenstrukturanalyse*, Bd VIII, Springer-Verlag, Berlin, 1958, viii + 204 S., Steif geheftet DM 28.—

H. Bredereck und E. Muller, *Organische Chemie in Einzeldarstellungen*. VI. Bd, *Präparative organische Photochemie*, Ankündigung des Springer-Verlages, Berlin, 1958, Etwa 288 S., Ganzleinen etwa DM 58.—

Schulze, *Molekülbau*, Slg. Göschen Bd 786, Walter de Gruyter und Co., Berlin, 1958, 123 S., geh. DM 2.40

H. Sirk, *Einführung in die Vektorrechnung für Naturwissenschaftler und Chemiker*, Verlag Dr. Dietrich Steinkopff, Darmstadt, 1958, x + 124, DM 16.—

Anon., *Analyse-Voorschriften*, Kunststoffeninstituut T.N.O., Delft, 1958, loose-leaf publication (in Dutch), Dutch guilders 75.—.

Announcements

26e CONGRES INTERNATIONAL DE FONDERIE

L'Instituto del Hierro y del Acero, chargé par le Comité International des Associations Techniques de Fonderie de l'organisation du 26e Congrès International de Fonderie et par le Conseil Supérieur des Recherches Scientifiques d'Espagne, de sa IVe Assemblée Générale, a l'honneur de vous inviter à prendre part à ces deux actes.

Ce congrès aura lieu à Madrid du 4 au 10 octobre 1959. Le thème des mémoires scientifiques est libre. Le programme provisoire comprend:

> Séances solennelles d'ouverture et de clôture; Inauguration des nouvelles installations de l'Instituto del Hierro y del Acero à la Cité Universitaire; Présentation et discussion de mémoires; Réunions des Commissions Internationales de Fonderie; Conférences techniques; Réceptions officielles; Visites de fabriques; Soirées artistiques; Programme spécial pour dames; Voyage post-Congrès d'intérêt technique et touristique, avec deux itinéraires: Espagne du Nord; Espagne du Sud et Méditerranée.

Nous espérons vous souhaiter la bienvenue à Madrid en 1959 et votre rendre séjour en Espagne agréable et instructif.

L'Agence Wagons-Lits/Cook, a été chargée officiellement de l'organisation de voyages et de logements.

Toute information sera fournie avec plaisir par l'Instituto del Hierro y del Acero, 13 Villanueva, à Madrid.

PRELIMINARY NOTICE
# of the
2nd INTERNATIONAL CONGRESS OF POLAROGRAPHY
Organised by the
POLAROGRAPHIC SOCIETY

to be held in Cambridge 24th—29th August 1959.

The Congress will be held in the University of Cambridge and will consist of Scientific Sessions (original papers, reviews and discussions) and Exhibition of Commercial Equipment, Demonstrations of Laboratory Apparatus, visits to local industry and places of interest and social functions.

A supporting programme for ladies is being arranged.

The scientific programme will be divided into the following Sections:

1. Instrumentation.
2. Theory and Kinetics.
3. Analytical and Industrial Applications.
4. Fundamental Studies.
5. Biological and Medical Applications.
6. Miscellaneous.

There will also be four Plenary Lectures by World Authorities and six Section Lectures. Contributions will be welcome and details should be submitted to: G. F. REYNOLDS, M.Sc., F.R.I.C., Chemical Inspectorate, Ministry of Supply, C. 36. Royal Arsenal, Woolwich, London, S.E.18, (Great Britain)

Notification of intention to submit a communication should be made as soon as possible and in anycase not later than 31st, March 1959, by which date a summary not exceeding 200 words is also required. Preprints of all papers will be issued and final manuscripts must therefore be received not later than 31st, May 1959. There will be an exhibition of commercial equipment and ancilliary materials.

Requests for application forms and further details should be sent to: Mrs. B. LAMB B.Sc., F.R.I.C., Chemistry Laboratory, Evershed and Vignoles, Corner of Iveagh Avenue, North Circular Road, London, N.W.10 (Great Britain).

SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM WITH 1-NAPHTHYLAMINE-4,6,8-TRISULFONIC ACID

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INTRODUCTION

In 1956 1-naphthylamine-3,5,7-trisulfonic acid was reported by this laboratory as a new reagent for the spectrophotometric determination of trace amounts of osmium[1]. The compound is more sensitive than the various thioureas previously reported for this determination. In addition to its higher sensitivity, the new reaction is carried out in weakly acid medium instead of in strong acid required in the thiourea methods. The chief disadvantage of the new method is that osmium must be in the osmate (OsVI) state of oxidation and 4 hours are required for maximum color development.

Recently we have investigated this reaction more fully[2] and found that by selecting the proper naphthylamine sulfonic acid isomer, adjusting the pH, and maintaining the proper temperature; the time required for complex formation is substantially reduced and the sensitivity slightly increased.

The reaction between 1-naphthylamine-4,6,8-trisulfonic acid and osmium, as the osmate ion, was investigated fully to determine whether the color produced could be utilized as the basis for a convenient, sensitive, and quantitative spectrophotometric method of analysis for trace amounts of osmium. The compound may also be used for ruthenium.

APPARATUS

All absorbance measurements were made with a Beckman spectrophotometer, Model DU, using matched 1.000-cm Corex cells. At wavelengths of 625 mμ or below, the ultraviolet-sensitive phototube was used; above 625 mμ, the red-sensitive phototube. The phototube circuit was kept at maximum sensitivity and under these conditions the slit width at 560 mμ was about 0.035 mm, corresponding to a band width of approximately 2 mμ.

A Beckman pH meter, Model G, was used for all pH measurements. The meter was calibrated daily with Fisher Certified Standard Buffers.

Temperature bath, accurate to ± 0.2°C.

The osmium still is essentially that of WESTLAND AND BEAMISH[3] with only a few minor changes[2].

REAGENTS

Standard osmium solutions

Solutions containing 100 p.p.m. osmium were prepared by dissolving 0.0194 g of potassium osmate ($K_2OsO_4 \cdot 2H_2O$), obtained from the American Platinum Works, in distilled water and diluting to the mark in 100-ml volumetric flasks. According to FRIEND[4] this solution is stable, but for maximum stability it is best stored in a refrigerator.

Reagent solution

1-naphthylamine-4,6,8-trisulfonic acid was purified by dissolving in a minimum amount of warm water and precipitated by the addition of isopropyl alcohol. Recrystallizations were continued until a solution gave the constant break in the mole-ratio determination experiment. The number of recrystallizations required varies from 1 to 5 depending upon the purity of the compound. After purification, the reagent solution is prepared by dissolving the required amount in distilled water. The reagent may be obtained from the LaMotte Chemical Products Company, Chestertown, Md. (U.S.A.).

Buffer solution

A buffer solution (Clark and Lubs type) was prepared by mixing 97 ml of 0.2*N* HCl and 50 ml 0.2*N* KCl and diluting to 200 ml. The pH is 1.0.

Other reagents

All other reagents were analytical grade and were used without further purification.

EXPERIMENTAL

Effect of pH

Osmium, as the osmate (OsVI), reacts with 1-naphthylamine-4,6,8-trisulfonic acid to produce a water-soluble purple complex which changes to violet as the pH-1.0 buffer is added. The effect of the hydrogen-ion concentration on the absorbance of the complex was studied using a solution containing 3.55 p.p.m. osmium, excess reagent, and varying amounts of hydrochloric acid and sodium hydroxide. The results are given in Fig. 1 and show a maximum absorbance at 555 mμ with a pH between 1.0 and 1.5. It was found that 10 ml of pH-1.0 buffer per 25-ml aliquot is sufficient to give reproducible results. The purple color that forms at pH 3 changes to light blue at pH 6 and finally to a pale green above pH 8. Varying the hydrogen-ion concentration has no effect on the absorbance of the reagent at 555 mμ.

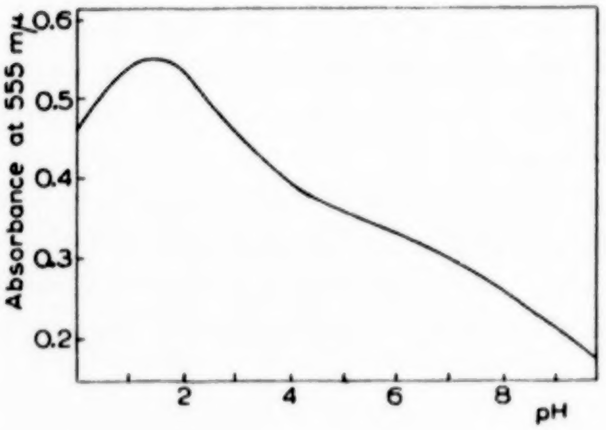

Fig. 1. Absorption *versus* pH for a 3.55 p.p.m. solution of osmium as the complex.

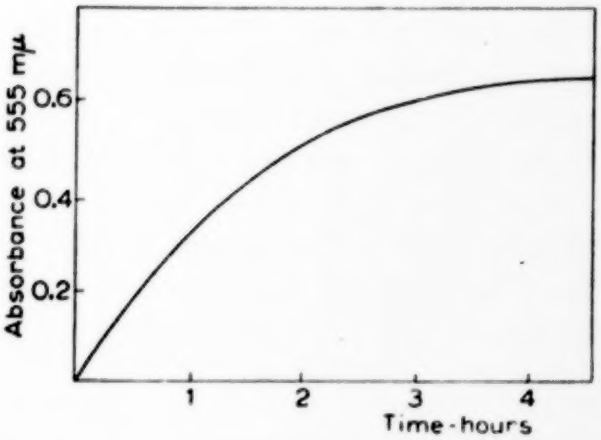

Fig. 2. Rate of complex formation *versus* time at 15°.

Stability of the complex

Absorbance measurements of a solution containing 4 p.p.m. osmium, excess reagent, and pH-1.0 buffer showed no appreciable change over a period of one month at room temperature. At 50° solutions of the complex are stable for 10 hours. The complex is destroyed by oxidizing agents such as hydrogen peroxide and sodium hypochlorite. An ethanol solution of the complex shows a slight decomposition after 12 hours at room temperature. Evaporation of an aqueous solution of the complex yields long monoclinic purple needles. A solution of the crystals shows a loss in absorbance (approx. 10%) indicating partial decomposition.

Effect of reagent concentration

A study was made to determine the effect of the reagent concentration on the absorbance of the system. It was found that if enough reagent is present to complex all of the osmate ions, a further increase in the concentration does not produce a significant change in the absorbance value at 555 mμ. After standing a month some decomposition products begin to appear which absorb slightly at the maximum of the complex. For this reason, any reagent solution more than a month old should be limited to a 4 to 1 ratio of reagent to osmate ion.

Rate of color formation

The rate of color formation was investigated using an osmate solution containing 4 p.p.m. osmium, excess reagent and varying amounts of hydrochloric acid and sodium hydroxide. The rate was found to be dependent on two factors, namely, the temperature of the solution and the pH.

Holding the pH constant at 2.0 ± 0.1 solutions of osmate and reagent were kept at 15° for varying periods of time, then diluted with 10 ml of pH-1.0 buffer, made up to the mark with water and the absorbance measured at 555 mμ. The results are given in Fig. 2 and show that 4 h are required for maximum color development.

Runs were also made at 20°, 25°, 30°, 35°, 40° and 45°. Fig. 3 is a plot of absorbance *versus* temperature at the end of 1 h. It is seen that the reaction is practically complete at the end of 1 h at 35°. Higher temperatures were avoided to eliminate any chance of destroying the complex. 45 min at 40° is recommended.

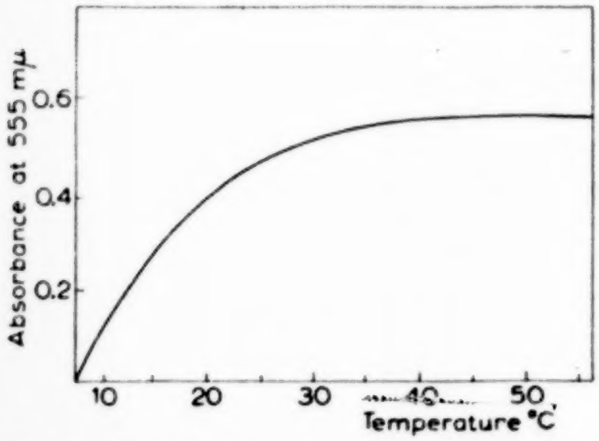

Fig. 3. Complex formed *versus* temperature at 1 hour.

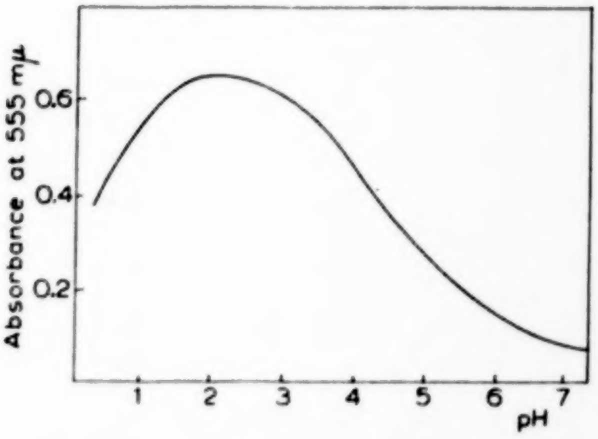

Fig. 4. Rate of complex formation *versus* pH at 35°.

Maintaining a constant temperature at 35°, solutions containing 4 p.p.m. osmium, excess reagent and varying hydrogen ion concentrations were allowed to react for 1 h. The solutions were then diluted with 10 ml of pH-1.0 buffer and water added to the mark. Absorbance readings were taken at 555 mμ. Fig. 4 shows that the solution must have a pH 1.5 to 2.5 for maximum rate of color formation.

Beer's law

In order to determine whether or not the system obeys Beer's law, a calibration curve was prepared. A series of solutions containing varying amounts of osmate ions and excess reagent, were allowed to react completely and then pH-1.0 buffer was added.

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Absorbance measurements were made against a reagent blank at 555 mμ, and a plot of the data was made. In the absence of interfering substances, the complex concentration is proportional to the absorbed radiant energy between the concentration limits of $5.2 \cdot 10^{-7}$ and $3.4 \cdot 10^{-5} M$ osmium (0.1 to 6.5 p.p.m. osmium) as indicated by a straight line over this range.

SUGGESTED METHOD FOR DETERMINING OSMIUM(VI) IN ABSENCE OF INTERFERING SUBSTANCES

Pipette 5 ml of $5 \cdot 10^{-4} M$ reagent in the solution of osmate ions in a 25-ml volumetric flask and add 0.1 N hydrochloric acid dropwise until slightly acid (pH 2.5–3). Warm in a water bath at 40° for 45 min, then add 10 ml of pH-1.0 buffer and dilute to the mark with distilled water. Measure the absorbance at 555 mμ and convert absorbance units to osmium concentration with the aid of a previously prepared calibration curve.

Sensitivity and applicability of the method

At 555 mμ the molar absorptivity of the system is $2.98 \cdot 10^4$ liters·moles^{-1}·cm^{-1}. This corresponds to a sensitivity of 0.0068 μg/cm², *i.e.*, 1 part of osmium in 140,000,000 parts of solution. A more practical value, however, is one in 20,000,000 because this value is reproducible within the limits of accuracy of the method.

A series of 10 determinations is given in Table I. The results show that the method is accurate to ± 2% over the concentration range $5.2 \cdot 10^{-7}$ to $5.2 \cdot 10^{-5} M$ osmium provided no interfering ions are present. Concentrations greater than $6 \cdot 10^{-5} M$ absorb too strongly at 555 mμ to be measured accurately.

TABLE I

RESULTS OF SEVERAL DETERMINATIONS

Reagent = $1 \cdot 10^{-4} M$: pH = 1.5

Concentration of Osmium (VI) in p.p.m		
Added	*Found*	*Error %*
0.01	0.02	+100
0.05	0.06	+ 10
0.10	0.11	+ 2
0.50	0.51	+ 2
1.00	1.00	0
2.00	2.02	+ 1
3.00	3.00	0
4.00	3.87	— 0.8
6.00	6.07	+ 1.2
8.00	7.94	— 0.8

Accuracy and precision of the method

From the data in Table I it is apparent that the optimum concentration is between 0.1 and 8 p.p.m. osmium. The standard deviation was determined by preparing a set of solutions containing 4 p.p.m. osmium and excess reagent, heating at 40° for 45 min, adding pH-1.0 buffer and measuring the absorbance at 555 mμ. The data are given in Table II.

The absorbance value from the calibration curve is 0.620 abs. unit.

TABLE II

RESULTS OF PRECISION AND ACCURACY DETERMINATIONS

Solution	*Abs. at 555 mμ*	*Deviation*	*(Deviation)² × 10⁶*
1	0.621	0.001	1
2	0.620	0.002	4
3	0.620	0.002	4
4	0.622	0.000	0
5	0.625	0.003	9
6	0.622	0.000	0
7	0.623	0.001	1
8	0.621	0.001	1
9	0.623	0.001	0
10	0.622	0.000	0
	Av. 0.622	Total	21

Std. deviation 0.002 abs. unit, *i.e.*, 0.013 μg osmium

Effect of diverse ions

The specificity of the reaction was determined by preparing a solution containing 4 p.p.m. osmium, developed under optimum conditions, and varying amounts of the ionic species in question. An increase or decrease of 0.005 absorbance unit was taken as interference. The following ions were found to interfere in concentrations of 1:1 or less: RuO_4^{-2}, Ru^{+3}, Rh^{+3}, Ir^{+4}, Pd^{+2}, Pt^{+4}, Al^{+3}, V^{+2}, Cr^{+3}, Fe^{+3}, Fe^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Pb^{+2}, Mn^{+2}, Mg^{+2} and Hg_2^{+2}. The results show that the reaction is not specific and that osmium must be separated from many common substances before it can be determined by this method.

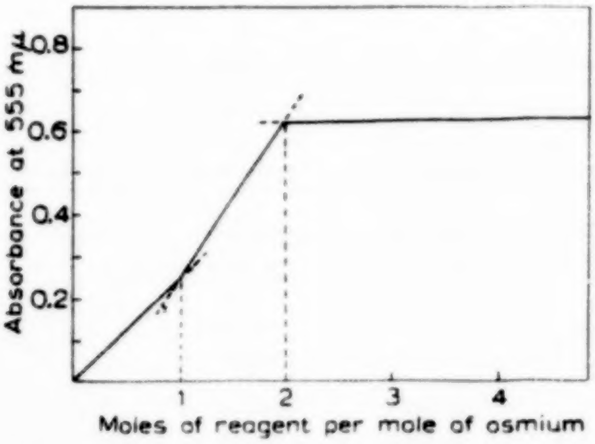

Fig. 5. Mole-ratio method applied to the osmium complex.

Nature of the complex in solution

Three methods were used to establish the empirical formula of the complex *in solution*. These were the mole-ratio method of YOE AND JONES[5], continuous variations method of JOB modified by VOSBURG AND COOPER[6] and the slope-ratio method of HARVEY AND MANNING[7]. Results of the three methods indicate a ratio of 2 moles of the reagent to 1 mole of the metallic ion. The mole-ratio curve in Fig. 5 indicates that with *excess* osmate ions a 1:1 complex is formed; the latter rapidly changes to the more stable 2:1 species as more reagent is added.

THE SEPARATION OF OSMIUM

Place the sample of osmium in the distillation apparatus[2,3] and regulate the flow of air so that, while the sample is being dissolved and during the distillation, the entire apparatus is continually swept with scrubbed air. Next, add $6N$ nitric acid, by means of the stopcock at the top of the distilling flask, until the sample just dissolves. Many alloys and some compounds containing osmium are not directly soluble in $6N$ nitric acid and must first be fused with ammonium persulfate or sodium peroxide. After the reaction has stopped, add more nitric acid (25 ml total) and slowly heat to boiling. Continue boiling for 30 min, distilling the osmium tetraoxide into the receiver containing 25 ml of $0.05N$ potassium hydroxide. Remove the basic distillate and analyze according to the procedure as outlined previously.

For small concentrations of osmium (less than 0.1 mg) the tetraoxide can be collected in 5 ml of $0.05N$ potassium hydroxide and thus increase the overall sensitivity of the method.

Results of analysis

Samples 1 through 5 were prepared by adding varying amounts of osmium to solutions, each containing approximately 1 mg of the following ions: Fe^{+3}, Cu^{+2}, Ni^{+2}, Co^{+2}, Pt^{+4}, Ir^{+4}, Ru^{+3}, Rh^{+3}, and Pd^{+2}. Samples 6 through 10 contained 1 mg Ru^{+3} and varying amounts of osmium. The samples were then treated with zinc dust and sulfuric acid to insure the lower oxidation state of osmium. No alloys were available to test the persulfate fusion, so this reagent was added to the reduced samples.

After the distillation was complete, aliquots of the basic distillate were pipetted into 25-ml volumetric flasks, neutralized and analyzed according to the proposed method.

The results of the ten distillations are given in Table III.

TABLE III

DISTILLATION OF OSMIUM

Sample	*Os added (mg)*	*Os found (mg)*	*% Recovery*
1	0.010	0.009	90
2	0.10	0.09	90
3	0.20	0.20	100
4	0.20	0.19	95
5	0.50	0.48	96
6	0.50	0.49	98
7	0.50	0.48	96
8	0.50	0.50	100
9	1.00	1.01	101
10	1.00	1.00	100

SUMMARY

This investigation was undertaken to determine if the naphthylamine sulfonic acid–osmate (OsVI) reaction is suitable for a spectrophotometric determination of osmium. The 1-naphthylamine-4,6,8-trisulfonic acid–osmate complex is water-soluble and forms a stable violet-colored system at pH 1 to 1.5 that is independent of reagent concentration. At 555 mμ the colored complex obeys Beer's law over a concentration range of 0.1 to 6.5 p.p.m. osmium and remains stable with respect to time and temperature. The effects of pH, temperature, reagent concentration, and diverse ions were studied. The nature of the organo–osmate complex *in solution* was studied by three techniques and the effect of temperature and pH on the rate of complex formation was

determined. A procedure for the removal of osmium from all interfering ions was developed based on well known distillation techniques.

A convenient, sensitive, reproducible and accurate method for the spectrophotometric determination of osmium has been developed.

RÉSUMÉ

Les auteurs ont étudié la réaction entre l'acide amino-1-naphtalène trisulfonique-4,6,8 avec l'osmium(VI). On obtient un complexe violet, stable, permettant un dosage spectrophotométrique de l'osmium à 555 mμ, pour des teneurs allant de 0.1 à 6.5 p.p.m. Une méthode de séparation de l'osmium d'avec les éléments gênants est proposée, en utilisant une technique par distillation.

ZUSAMMENFASSUNG

Die Reaktion zwischen Osmium-(VI) und 1-Amino-naphtalin-4,6,8-trisulfosäure wird als Grundlage zu einer spektrophotometrischen Bestimmung des Osmiums vorgeschlagen. In der Form des violetten Komplexes lässt sich das Osmium bei 555 mμ in einem Konzentrationsbereich von 0.1 bis 6.5 p.p.m. bestimmen. Die Abtrennung des Osmiums von störenden Metallen kann durch ein Destillationsverfahren erfolgen.

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SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM WITH 1-NAPHTHYLAMINE-3,5,7-TRISULFONIC ACID

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INTRODUCTION

During a recent investigation of the naphthylamine sulfonic acid–osmate (OsVI) reactions, it was observed that additional chemical evidence might be obtained using the ruthenate ion[1]. It was thought that since many of the reactions of osmium and ruthenium are similar, the formation of a ruthenate–naphthylamine sulfonic acid complex would add much to our information concerning a reaction mechanism.

After studying several of the ruthenium complexes, the reaction between 1-naphthylamine-3,5,7-trisulfonic acid and ruthenium was investigated fully to determine the applicability of the color produced as the basis for a convenient, sensitive, and quantitative spectrophotometric method of analysis for trace amounts of ruthenium. The 4,6,8-isomer may be used equally well.

APPARATUS

All absorbance measurements were made with a Beckman spectrophotometer, Model DU, using matched 1.000-cm Corex cells. At wavelengths of 625 mμ or below, the ultraviolet-sensitive phototube was used; above 625 mμ, the red-sensitive. The phototube circuit was kept at maximum sensitivity and under these conditions the slit width at 530 mμ was about 0.035 mm, corresponding to a band width of approximately 2 mμ.

A Beckman pH meter, Model G, was used for all pH measurements. The meter was calibrated daily, using Fisher Certified Standard Buffers.

Temperature bath, accurate to ± 0.2°C.

The ruthenium still is essentially that of WESTLAND AND BEAMISH[2] with only a few changes[1].

REAGENTS

Standard ruthenium solutions

A solution of ruthenium chloride ($RuCl_3$) obtained from the American Platinum Works, was standardized by precipitating the ruthenium as the hydrated oxide and weighing as the oxide (Ru_2O_3). Unless the solution is acid, the ruthenium(III) will slowly undergo hydrolysis.

Reagent solution

1-naphthylamine-3,5,7-trisulfonic acid was purified by dissolving in a minimum amount of warm water and precipitated by the addition of isopropyl alcohol. The reprecipitations were continued until a solution of the reagent gave a constant break in a mole-ratio determination with a standard osmate solution. The number of recrystallizations necessary vary from 1 to 5 depending upon the state of purity of the compound available. After purification, the reagent solution is prepared by dissolving the required amount in distilled water. The reagent may be obtained from the LaMotte Chemical Products Company, Chestertown, Md. (U.S.A.).

Buffer solutions

Buffer solutions were the Clark and Lubs type, prepared by mixing 97 ml of 0.2N HCl and 50 ml 0.2N KCl and diluting to 200 ml. The pH is 1.0.

Other reagents

All other reagents were analytical grade and used without further purification.

EXPERIMENTAL

Absorbance curve

An absorbance curve of the reagent solution ($5 \cdot 10^{-4}M$) and of the ruthenate complex ($1.96 \cdot 10^{-4}M$) is shown in Fig. 1. Measurements were taken every 10 mμ except

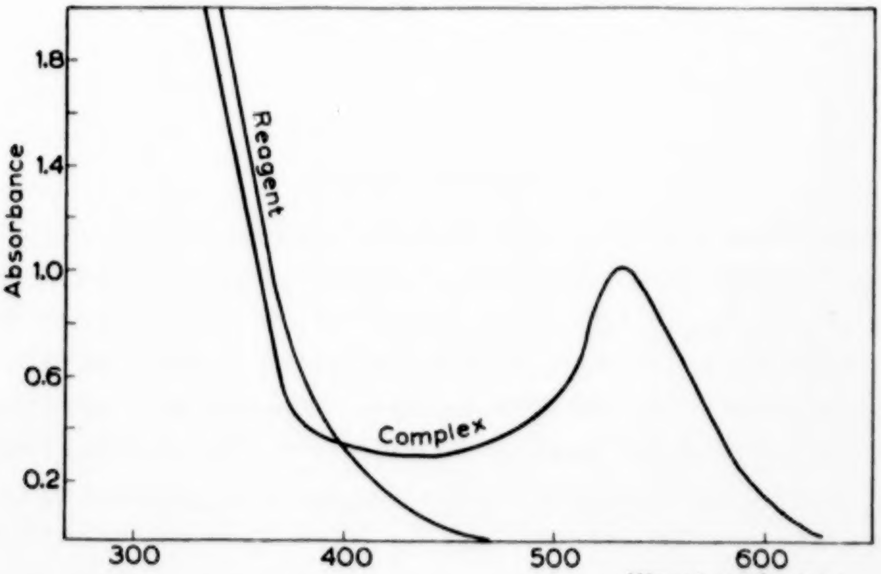

Fig. 1. Absorption spectra of reagent ($5 \cdot 10^{-4}M$) and its ruthenium complex ($1.96 \cdot 10^{-4}M$).

where maxima were encountered, then the readings were taken every 5 mμ. All measurements were made against a water blank, since the absorbance of the reagent at the maxima of the complex is negligible. Experiments show that a tolerance of 7-fold excess reagent is possible. The curve for the complex shows a sharp peak at 530 mμ.

Effect of pH

The effect of the hydrogen-ion concentration on the absorbance of the organo-ruthenate complex was studied using a $1.96 \cdot 10^{-4} M$ solution complex, excess reagent and varying quantities of hydrochloric acid and sodium hydroxide. As shown in Fig. 2, the maximum absorbance is at 530 mμ with a pH between 1.0 and 3.0. It was found that 10 ml of pH-1 buffer per 25-ml aliquot was sufficient to give reproducible results. Varying the hydrogen-ion concentration has no effect on the absorbance of the reagent at 530 mμ.

Rate of color formation

Unlike the osmate–naphthylamine sulfonic acid reaction[1] the ruthenate reacts almost instantaneously, when the pH is between 2.5 and 5. Above pH 7 and below pH 1.5 the complex is not formed.

Temperature has little noticeable effect on rate of complex formation since the reaction is rapid even at 15°.

Beer's law

The organo–ruthenium complex adheres to Beer's law up to a ruthenium concentration range of 20 p.p.m. The optimum range for the absorbance measurements on the spectrophotometer is 0.2 to 0.7 units. With the procedure outlined, these values correspond to a ruthenium concentration of 3 to 14 p.p.m.

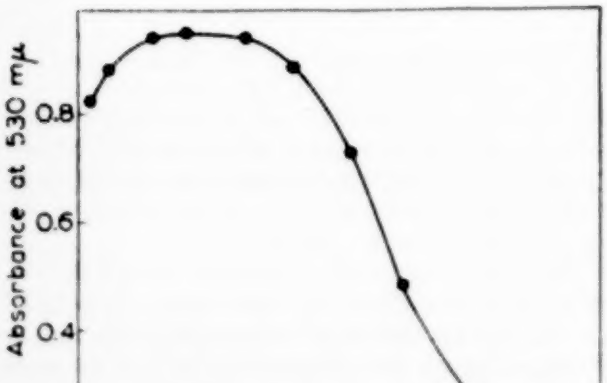

Fig. 2. Absorption *versus* pH for $1.96 \cdot 10^{-4} M$ solution of the ruthenium complex.

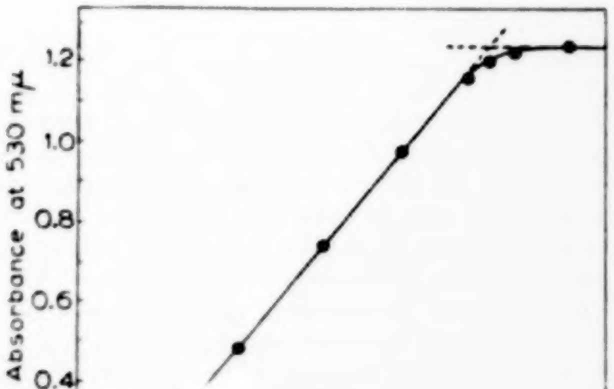

Fig. 3. Mole-ratio method applied to the ruthenium complex.

Sensitivity

According to SANDELL's[3] expression of sensitivity and using an absorbance value of 0.201 unit for a 4 p.p.m. ruthenium solution, the sensitivity is 0.02 μg/cm^2. For general use, however, the practical sensitivity is 0.1 μg/cm^2, *i.e.*, 1 part of ruthenium in 10,000,000 parts of solution.

Effect of order of adding solutions

As long as the ruthenium is in the valence state of the ruthenate ion, and the reagent solution is acid enough to have a proton on the amine group, the order of mixing is immaterial. It is essential, however, to maintain a pH during the reaction which will prevent the decomposition of the ruthenate ion, *i.e.*, pH 2.5 to 5.

Nature of the complex in solution

The empirical formula of the ruthenate complex was checked by the mole-ratio method of YOE AND JONES[4]. Since the procedures of analysis and reaction mechanism are so similar to the osmate system[1], it was felt that continuous variations and slope-ratio determinations would be unnecessary additions to the evidence already accumulated for the system. Fig. 3 shows the straight-line relationship between the absorbance and the amount of ruthenium added until the concentration reaches one-half that of the reagent. At this point, a sharp break occurs in the curve indicating no further complex formation. Hence, the formula of the complex is R_2RuO_4.

Effect of diverse ions

Because the mechanism of the proposed procedure eliminates all interfering materials known to interfere with the naphthylamine–osmate reaction, no systematic investigation of this effect was studied. It was found, however, that if these ionic species were added to the complex, an absorbance change was observed. If these substances were added to the distillation flask, no interference was noted in the procedure.

SUGGESTED METHOD FOR THE SEPARATION AND DETERMINATION OF RUTHENIUM

Place the sample in the distillation apparatus and dissolve it in 6N nitric acid. Boil the solution for 15 to 30 min to expel any osmium as the tetraoxide, add 20 ml of 0.1M $KMnO_4$ and again boil for 15 to 30 min depending upon the concentration of the ruthenium present. As in the case of osmium[5], ruthenium samples that do not dissolve in dilute nitric acid are first fused with $K_2S_2O_8$, Na_2O_2, or $KOH–KNO_3$ mixture and then treated with 6N nitric acid.

Collect the ruthenium tetraoxide that distills from the permanganate oxidation in 25 ml of $5 \cdot 10^{-4}M$ reagent solution (pH 2.5–3.0). After the ruthenium has been distilled and collected, add 5-ml aliquots of the organo–ruthenium complex to a 10-ml volumetric flask, dilute to the mark with pH-1 buffer, mix and measure the absorbance of the solution at 530 mμ against a reagent blank or a water blank. Read the ruthenium concentration from a preciously constructed absorbance *vs.* concentration graph (Beer's law curve).

For small concentrations of ruthenium (0.05 to 0.005 mg) the tetraoxide can be collected in 5 ml of the reagent solution to increase the overall sensitivity of the procedure.

Accuracy and precision of the method

6 samples containing 0.5 mg of ruthenium and varying quantities of osmium, were

distilled according to the previous section. Standard deviations for the distillation of ruthenium were determined by measuring the absorbance of the ruthenate complex formed after the osmium was boiled off. Table I shows the result of the 6 samples. The absorbance value for the concentration of ruthenium measured (10 p.p.m.) as taken from the Beer's law curve is 0.487 abs. unit.

TABLE I

Sample	*Ru added (p.p.m.)*	*Os added (mg)*	*Abs. at 530 mμ*	*Ru found (p.p.m.)*	*(Deviations)*^{2} $\times$ *10*^{4}
1	10.00	0.10	0.484	9.94	9
2	10.00	0.20	0.482	9.90	25
3	10.00	0.30	0.493	10.12	36
4	10.00	0.50	0.491	10.08	16
5	10.00	0.70	0.483	9.92	16
6	10.00	1.00	0.487	10.00	0

S.D. = 0.004 Abs. unit, *i.e.*, 0.08 μg Ru.

SUMMARY

An investigation has been made to determine the applicability of the osmate–naphthylamine reaction to the ruthenate system. It was found that under proper conditions, ruthenium (RuVI) reacts with 1-naphthylamine-3,5,7-trisulfonic acid to form a water-soluble red complex ion with a maximum absorbance at 530 mμ. The complex was found to be stable and to obey Beer's law over a concentration range of 0.5 to 14 p.p.m. The effects of pH, reagent concentration, and diverse ions were studied. The nature of the complex in solution was investigated, and a standard procedure for analysis recommended. A procedure for the removal of ruthenium from all interfering materials was developed based on well known distillation techniques.

A rapid, sensitive, reproducible and accurate method for the spectrophotometric determination of ruthenium has been developed.

RÉSUMÉ

Une méthode spectrophotométrique est proposée pour le dosage du ruthénium au moyen de l'acide amino-1-naphtalène trisulfonique-4,6,8. On obtient un complexe stable, rouge, ayant une absorption maximum à 530 mμ. On sépare le ruthénium d'avec les éléments gênants par distillation.

ZUSAMMENFASSUNG

Die Reaktion zwischen Ruthenium und 1-Amino-naphtalin-4,6,8-trisulfosäure wird als Grundlage zu einer spektrophotometrischen Bestimmung des Rutheniums vorgeschlagen. Die erhaltene rote Komplexverbindung besitzt ein Absorptionsmaximum bei 530 mμ. Das Ruthenium wird von störenden Elementen durch ein Destillationsverfahren abgetrennt.

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A RAPID AND PRECISE MICRO-HETEROMETRIC DETERMINATION OF GOLD, PALLADIUM OR PLATINUM WITH NITRON IN THIOCYANATE SOLUTIONS

A STUDY OF THE REACTIONS AND OF THE COMPOUNDS

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INTRODUCTION

Nothing seems to be known about the reactions between the thiocyanato-complexes of gold(III), palladium or platinum(IV) and nitron. All three metal chlorides gave coloured solutions in the presence of excesses of potassium thiocyanate: gold gave an intense tea brown solution, palladium an orange one and platinum a yellow solution. The colour of the palladium and platinum solutions did not fade on dilution, whereas the gold solution became colourless under these conditions. Ammonia immediately decolourized the palladium thiocyanato-complex, but the corresponding platinum complex was less sensitive to the addition of ammonia. On the addition of nitron to the metal chloride solutions, *in the absence of thiocyanate*, no noticeable change occurred in the palladium or platinum solutions, which remained clear. In the case of gold chloride, a small amount of a flocculent yellowish precipitate appeared in hydrochloric acid solution; however, no change took place in sodium acetate solution.

Entirely different reactions were obtained when the heterometric reaction with nitron was carried out in the presence of *excesses of potassium thiocyanate*. Almost independently of the pH, insoluble compounds were obtained with all three metals. The compounds could be used for a *rapid* and *precise* heterometric determination of traces of each of the above metals. Ten minutes was entirely sufficient, in all normal cases, for a complete titration of these metals. Normally the error was between zero and 1%. The molar sensitivity of the reaction was approximately the same for all three metals (concentrations: $2 \cdot 10^{-4} M$ $PdCl_2$, $3 \cdot 10^{-4} M$ $AuCl_3$ and $4 \cdot 10^{-4} M$ H_2PtCl_6). The determination of palladium with nitron was more sensitive than any other heterometric method presented previously[1]. The amounts of the metals necessary for the analyses (in 20 ml solution) were about 1 mg gold, 0.8–1.6 mg platinum and 0.4 mg palladium.

It was very interesting to establish that, in the presence of potassium thiocyanate, even chloroplatinic acid reacted immediately with nitron, quantitatively giving an insoluble compound of definite composition. Another interesting feature was the remarkable insensitivity of the insoluble compounds obtained towards the most common complexing agents such as citrate, polyphosphates and ethylenediaminetetraacetate, at all pH's between 1 and 9. In contrast, potassium cyanide, when present in basic solution, dissolved all the insoluble compounds. In addition, the insoluble palladium compounds were dissolved in dilute ammonia; the platinum compounds required more concentrated ammonia for their solution. The gold compound gave an insoluble thiocyanato-complex of different composition in the presence of a large excess of ammonia. Besides the analytical study of the reaction, the composition of each of the compounds obtained was thoroughly investigated. The properties of all the compounds obtained and their structures will be discussed in a separate report.

EXPERIMENTAL

The same working conditions were observed as in previous heterometric investigations. The principles of heterometry have been discussed briefly in ref.[2]. Experience in dealing with problems in heterometry can be gained by studying the previous heterometric investigations, which were concerned with the study of complex compounds, of intermediates and of reactions in suspensions in general, as well as with the application of heterometry to microanalysis[3].

All chemicals used in this work were either AnalaR or chemical pure reagents. The special solutions were prepared as follows:

Nitron. (M.W. = 312.16) 0.7802 g nitron (Eastman Organic Chemicals, for chemical purposes) + 7 ml *M* CH_3COOH were dissolved in water to give 250 ml aqueous solution (= 0.01 *M*).

Palladium chloride (Johnson Matthey). 1 g $PdCl_2$ + 56 ml *M* HCl were dissolved in water to give a volume of 562.8 ml (= 0.01 *M*).

Gold chloride (brown) B.D.H. Laboratory reagent. 1 g $HAuCl_4 \cdot 3H_2O$ + 25 ml *M* HCl were dissolved in water to give a volume of 250 ml (approx. 0.01 *M* $HAuCl_4$/0.1 *M* HCl).

Chloroplatinic acid, $H_2PtCl_6 \cdot 6H_2O$, B.D.H. 1 g of the reagent was dissolved in water to give 500 ml solution (approx. 0.004 *M*).

More dilute solutions were prepared from these standard solutions. In the case of nitron the diluted solutions were freshly prepared every few days and all the solutions were kept in dark brown bottles.

RESULTS AND DISCUSSION

General

The heterometric reaction of the chlorides of the noble metals with nitron in the presence of excesses of potassium thiocyanate, was studied at different pH's in the presence and in the absence of complexing agents. A selection of experiments, the composition of the solutions and the results obtained are compiled in Tables I, II and III. The course of the heterometric titrations in a few experiments is presented in Fig. 1. The same numeration is used in both cases. In Table IV and in Fig. 2 a selection of heterometric titrations is presented in which the noble metals were present in solution in a mixture. The aim was to see how far each of the metals present could be determined by a heterometric titration.

Reverse titrations, in which solutions of the noble metals were used as titrants, were also performed. These titrations were carried out with the purpose of obtaining further insight into the different complex compounds formed during these titrations. The information gathered did not provide much that was of value for the analytical aspect of the research.

A special study was carried out to determine palladium in the presence of large excesses of foreign metals. The results of this investigation will be presented separately.

Titrations of solutions of gold chloride

Compounds

In almost all cases the compound, which was calculated from the first maximum density point, had the exact composition $Au_1N_1\downarrow\downarrow$ (N = nitron). Only in solutions

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(text continued on p. 221)

TABLE I

Composition: *a* ml $PdCl_2$ + *b* ml KCNS + *c* ml supplements + ad 20 ml H_2O + *x* ml *nM* nitron.
T = 20°. Content Pd: 0.4268 mg; concn. $2 \cdot 10^{-4}M$.

Expt. No.	*PdCl₂*		*ml KCNS 2M*	*Supplements*	*Found*						
					*Nitron **						
	ml	*Molarity*			*ml*	*Molarity*	*Initial ppt. at ml*	*Max. density value*	*Titration time in min*	*% error*	*Remarks*
1	4	0.001	1	—	i 3.93 h	0.0015	0.2	0.69	7	1.7	Bright brown ppt. End-point at Pd_2N_3
2	4	0.001	3	—	i 4.01 h	0.0015	0.6	0.58	7	0.3	,, ,, ,, ,, ,, ,,
3	4	0.001	1	3 ml *M* HCl	i 3.98 h	0.0015	0.2	0.66	8	0.5	,, ,, ,, ,, ,, ,,
4	4	0.001	1	3 ml *M* CH_3COOH	i 4.00 h	0.0015	0.2	0.67	7	0.0	,, ,, ,, ,, ,, ,,
5	4	0.001	1	1 ml *M* NH_4NO_3	i 3.97 h	0.0015	0.4	0.64	9	0.7	,, ,, ,, ,, ,, ,,
6	4	0.001	1	1 ml *M* CH_3COONa	i 4.00 h	0.0015	0.2	0.78	7	0.0	,, ,, ,,
7	4	0.001	1	4 ml 0.25*M* H_3PO_4	i 4.00 h	0.0015	0.2	0.81	9	0.0	,, ,, ,,
8	4	0.001	1	2 ml 0.5*M* Na_2HPO_4	i 4.00 h	0.0015	0.0	0.74	7	0.0	,, ,, ,,
9	4	0.001	1	1 ml *M* Na_3-citrate	i 4.02 h	0.0015	0.0	0.86	5	0.5	Bright brown ppt. ,, ,, ,,
10	4	0.001	1	3 ml *M* Na_3-citrate	i 3.99 h	0.0015	0.2	0.69	7	0.3	,, ,, ,, ,, ,, ,,
11	4	0.001	1	3 ml *M* Na_2-tartrate	i 4.00 h	0.0015	0.4	0.73	5	0.0	,, ,, ,, ,, ,, ,,
12	4	0.001	1	8 ml 0.125*M* $Na_5P_3O_{10}$	i 4.01 h	0.0015	0.0	0.65	8	0.3	,, ,, ,, ,, ,, ,,
13	4	0.001	1	3 ml 0.2*M* Na_2-EDTA	i 4.00 h	0.0015	0.4	0.77	7	0.0	,, ,, ,, ,, ,, ,,
14	4	0.001	1	3 ml 0.2*M* Na_4-EDTA		0.0015	>5.0	0.0			
15	4	0.001	1	1 ml 0.2*M* KCN + 2 ml 0.5*M* Na_2HPO_4		0.0015	>5.0	0.0			
16	4	0.001	1	10 ml alcohol		0.0015	>5.0	0.0			
17	4	0.001	0.15	—	i 3.01	0.002	0.2	>0.40		0.3	Linear increase after the maximum
18	4	0.001	1	1 ml *M* NH_3		0.0015		0.0			
19	4	0.001	1	4 ml *M* NH_4NO_3	i.c. 3.00 h	0.002	0.0	0.69	5	0.0	End-point at Pd_2N_3
20	4	0.001	1	8 ml 0.125*M* $Na_4P_2O_7$	2.97	0.002	0.2	0.63	12	1.0	After the maximum linear increase

* i = intersection point; c = contact point; h = horizontal maximum density line.

TABLE II

Composition: *a* ml $HAuCl_4$ + *b* ml KCNS + *c* ml supplements + ad 20 ml H_2O + *x* ml *nM* nitron.

T = 20°. Content Au: 1.183 mg; concn. $3 \cdot 10^{-4}M$.

Expt. No.	*HAuCl₄*		*ml KCNS 2M*	*Supplements*	*Found*						
					Nitron *		*Initial ppt. at ml*	*Max. density value*	*Titration time in min*	*% error*	*Remarks*
	ml	*Molarity*			*ml*	*Molarity*					
21	3	0.002	—	—	? 2.6	0.002	~1.4	?0.18			Bright yellow floculant ppt.
22	3	0.002	—	1 ml *M* HCl	?	0.002	1.0	0.25	8		
23	3	0.002	—	1 ml *M* HNO_3	?	0.002	1.2	0.11	30		
24	3	0.002	—	1 ml *M* CH_3COONa		0.002	>5.0	0.0	5		
25	3	0.002	1	—	i 3.00 h	0.002	0.6	0.56	6	0.0	White ppt. End-point at Au_1N_1
26	3	0.002	5	—	i 3.05 h	0.002	0.8	0.50		1.7	Short horizontal line. White ppt.
27	3	0.002	1	1 ml *M* HNO_3	i 2.99 h	0.002	0.2	0.61	8	0.3	
28	3	0.002	1	1 ml *M* HCl	i 2.96 h	0.002	0.2	0.54	8	1.3	End-point at Au_1N_1
29	3	0.002	1	1 ml *M* CH_3COONa	i 2.99 h	0.002	0.4	0.62	9	0.3	,, ,, ,,
30	3	0.002	1	1 ml *M* Na_3-citrate	i 3.00 h	0.002	0.4	0.61	7	0.0	,, ,, ,,
31	3	0.002	1	2 ml 0.2*M* Na_2-EDTA	i 3.00 h	0.002	0.4	0.60	5	0.0	,, ,, ,, White ppt.
32	3	0.002	1	5 ml 0.2*M* Na_2-EDTA	i 3.00 h	0.002	0.4	0.57	5	0.0	,, ,,
33	3	0.002	1	2 ml 0.2*M* Na_2-EDTA + 2 ml 0.5*M* Na_2HPO_4	c 3.00 h	0.002	0.2	0.59	8	0.0	,, ,,
34	3	0.002	1	3 ml 0.2*M* Na_4-EDTA	>5.0	0.002	0.2	>0.50	5		Linear increase without intersection point
35	3	0.002	1	8 ml 0.125*M* $Na_4P_2O_7$	i 2.84	0.002	0.0	0.50	15		Linear increase after intersection
36	3	0.002	1	8 ml 0.125*M* $Na_5P_3O_{10}$	i 3.00 h	0.002	0.2	0.45	37	0.0	Short horizontal line, then linear increase
37	3	0.002	1	2 ml 0.2*M* Na_2-EDTA + 2 ml *M* NH_3	c 3.00 h	0.002	0.0	0.52	12	0.0	End-point at Au_1N_1. White ppt.
38	3	0.002	1	2 ml *M* NH_3 + 1 ml 0.5*M* NH_4NO_3	c 3.00 h	0.002	0.0	0.57	9	0.0	White gelatinous ppt.
39	3	0.002	1	0.5 ml conc. NH_3	i 4.50 h	0.002	0.2	0.75	9	0.0	End-point at Au_2N_3. Yellow ppt.
40	3	0.002	1	1 ml *M* KCN + 2 ml 0.5*M* Na_2HPO_4		0.002	>5.0	0.0			

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* i = intersection point; c = contact point; h = horizontal maximum density line.

TABLE III

Composition: *a* ml H_2PtCl_6 + *b* ml KCNS + *c* ml supplements + ad 20 ml H_2O + *x* ml *nM* nitron.

T = 20°. Content Pt: 1.5618 mg; concn. $4 \cdot 10^{-4}M$.

Expt. No.	H_2PtCl_6		*ml KCNS 2M*	*Supplements*	*Found*						
					Nitron *		*Initial ppt. at ml*	*Max. density value*	*Titration time in min*	*% error*	*Remarks*
	ml	*Molarity*			*ml*	*Molarity*					
41	2	0.004	1	—	i 2.98 h	0.002	0.0	0.66	8	0.7	End-point at Pt_4N_3 Yellow ppt.
42	4	0.002	5	—	i 2.99 h	0.002	0.4	0.79	7	0.3	,, ,, ,, ,, ,,
43	4	0.002	1	1 ml *M* HCl	i 2.97 h	0.002	0.0	0.72	8	1.0	,, ,, ,,
44	4	0.002	1	1 ml *M* CH_3COONa	i 3.00 h	0.002	0.2	0.62	12	0.0	Bright yellow powder
45	4	0.002	1	2 ml 0.5*M* Na_2HPO_4	c 3.0	0.002	0.0	0.57	5	0.0	End-point at Pt_4N_3
46	4	0.002	1	2 ml 0.2*M* Na_2-EDTA	i 3.02 h	0.002	0.0	0.80	8	0.7	,, ,, ,,
47	4	0.001	1	5 ml 0.2*M* Na_2-EDTA	c 3.0 h	0.001	0.4	0.33	9	0.0	End-point at Pt_4N_3. Fine yellow ppt.
48	4	0.002	1	3 ml 0.2*M* Na_4-EDTA	i 2.6	0.002	0.8	≫0.45	24		Intersection, then considerable linear increase
49	4	0.002	1	2 ml 0.2 *M* Na_2-EDTA + 2 ml 0.5*M* Na_2HPO_4	i 3.00 h	0.002	0.0	0.71		0.0	
50	4	0.002	1	1 ml *M* Na_3-citrate + 2 ml 0.5*M* Na_2HPO_4	c 3.00 h	0.002	0.0	0.60	6	0.0	
51	4	0.001	1	5 ml *M* Na_3-citrate	c 3.00 h	0.001	0.4	0.35	7	0.0	End-point at Pt_4N_3. Fine yellow ppt.
52	4	0.002	1	1 ml 0.2*M* KCN + 2 ml 0.5*M* Na_2HPO_4		0.002					Low density
53	4	0.002	1	2 ml *M* NH_3 + 5 ml 0.1*M* NH_4NO_3	i 2.97 h	0.002	0.0	0.66	10	1.0	Fine yellow ppt.
54	4	0.002	1	2 ml 2*M* pyridine	i 2.97 h	0.002	0.4	0.61	6	1.0	

* i = intersection point; c = contact point; h = horizontal maximum density line.

which contained large amounts of ammonia did the insoluble compound at the first maximum density point have the composition $Au_2N_3\downarrow\downarrow$.

In the absence of other metals

Table II, presents the composition of the solutions together with the results obtained (see Fig. 1). All titrations, which were carried out in the *absence of potassium thiocyanate*, gave low densities, the initial precipitation occurred very late and no end-point was reached (Expts. 21–24). Successful titrations could be carried out *only* in solutions that contained sufficient potassium thiocyanate (conc. approx. = 0.1*M*). Large *excesses of thiocyanate* made the end-point less certain (*cf.* Expts. 25 and 26). There were no essential differences between the results obtained in *nitric acid*, in *hydrogen chloride* or even in *sodium acetate* solutions (Expts. 27–29). Excesses of *Na$_3$-citrate* or *Na$_2$-EDTA* had no marked effect (Expts. 30–33). In the presence of excesses of Na$_4$-EDTA no end-point was reached (Expt. 34). The addition of excesses of polyphosphates caused an extension of the titration time and the end-point was less certain (Expts. 35–36). A *dilute ammonia* solution had hardly any influence on the end-point (Expts. 37 and 38). In the presence of a more *concentrated solution of ammonia* (conc. 0.4*M*) the

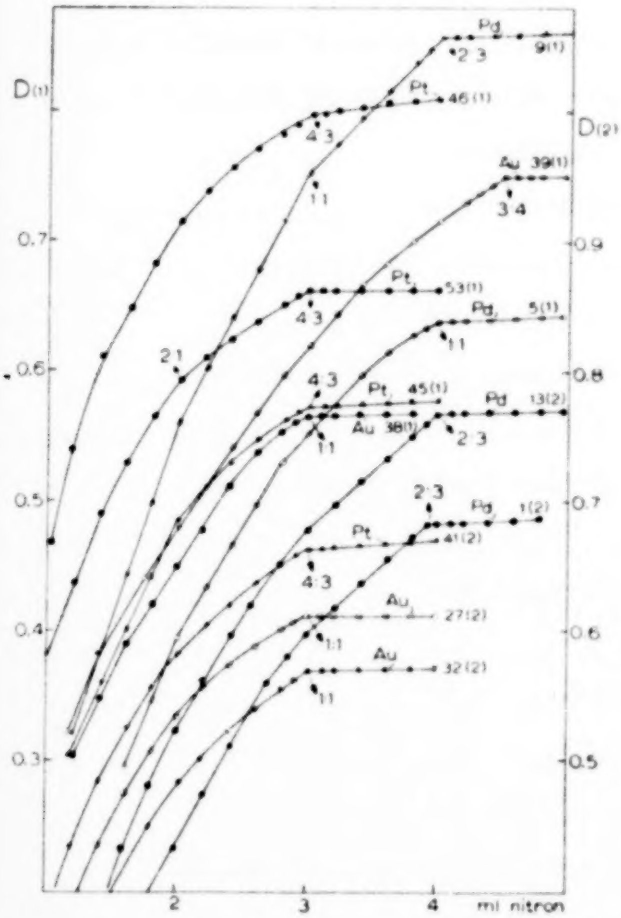

Fig. 1. Titrations of noble metal salts (= Me) with nitron (= N). Molar ratios [Me] : [N] at the critical points.

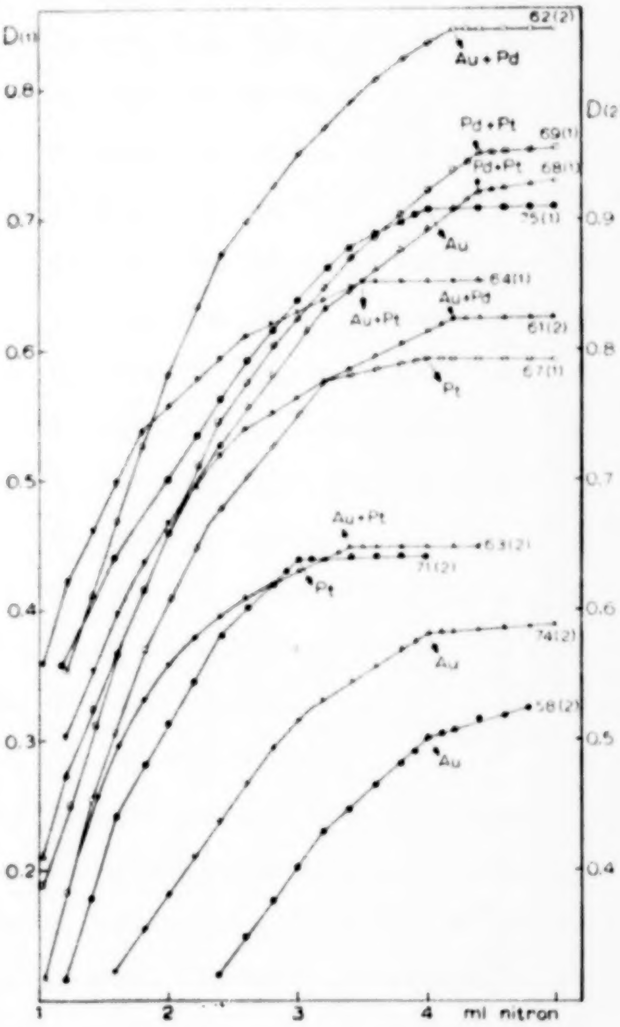

Fig. 2. Titrations of noble metal mixtures with nitron.

TABL

Composition: *a* ml metal salts + *b* ml KCNS + *c* ml supplemen

Expt. No.	*$HAuCl_4$*		*$PdCl_2$*		*H_2PtCl_6*		*ml 2M KCNS*	*Supplements*	
	ml	*Molarity*	*ml*	*Molarity*	*ml*	*Molarity*			*Au*
55	3	0.002	4	0.001	–	—	1	0.5 ml conc. NH_3	1.183
56	3	0.002	–	—	–	—	1	1 ml *M* NH_3 + 1 ml *M* NH_4NO_3	1.183
57	3	0.002	6	0.002	–	—	1	0.5 ml conc. NH_3 + 5 ml 0.2*M* Na_2-EDTA	1.183
58	3	0.002	6	0.002	–	—	1	1 ml 2*M* NH_3 + 5 ml *M* Na_3-citrate	1.183
59	3	0.002	–	—	2	0.002	1	0.5 ml conc. NH_3 + 3 ml 0.2*M* Na_2-EDTA	1.183
60	3	0.002	4	0.001	2	0.002	3	0.5 ml conc. NH_3 + 3 ml 0.2*M* Na_2-EDTA	1.183
61	2	0.002	3	0.001	–	—	1	3 ml *M* Na_3-citrate	0.788
62	2	0.002	3	0.001	–	—	1	3 ml 0.2*M* Na_2-EDTA	0.788
63	2	0.002	–	—	2	0.002	1	3 ml *M* Na_3-citrate	0.788
64	2	0.002			2	0.002	1	3 ml 0.2*M* Na_2-EDTA	0.788
65	3	0.002	–	—	2	0.002	1	0.5 ml conc. NH_3 + 3 ml *M* Na_3-citrate	1.183
66	–	—	6	0.002	4	0.002	1	1 ml *M* NH_3	
67	–	—	6	0.002	4	0.002	1	1 ml *M* NH_3 + 3 ml *M* Na_3-citrate	
68	–	—	2	0.002	2	0.002	1	—	
69	–	—	2	0.002	2	0.002	1	3 ml 0.2*M* Na_2-EDTA	
70	–	—	4	0.001	4	0.002	3	1 ml *M* NH_3	
71	–	—	6	0.002	4	0.002	1	1 ml *M* NH_3	
72	–	—	4	0.001	4	0.002	1	1 ml *M* NH_3	
73	3	0.002	–	—	3	0.002	1	0.5 ml conc. NH_3	1.183
74	3	0.002	5	0.002	2	0.002	3	0.5 ml conc. NH_3 + 3 ml 0.2*M* Na_2-EDTA	1.183
75	3	0.002	5	0.002	2	0.002	1	0.5 ml conc. NH_3	1.183

* = the metal determined; i = intersection point; c = contact point; h = horizontal maximu

titration took a different course: the reaction now became somewhat more sensitive towards gold and a higher maximum density value was obtained (Expt. 39). *The end-point was obtained at the point of quantitative formation of* Au_2N_3 ↓ ↓. The precipitate was of a yellow colour instead of white Au_1N_1 ↓ ↓. No precipitation at all occurred with nitron in the presence of excess potassium cyanide (Expt. 40). In most cases the *error* was close to zero. A normal titration lasted 5–10 minutes.

In mixtures

Table IV and Fig. 2 present some results of titrations of gold in mixtures with palladium or platinum or in mixtures containing both.

V

ad 20 ml H_2O + x ml nM nitron (= N). T = 20°.

ntent mg		*Found*						
		Nitron (x)		*Initial ppt. at ml*	*Max. density value*	*Titration time in min*	*% error*	*Remarks*
Pd	*Pt*	*ml*	*Molarity*					
426		i 4.50 h	0.002	0.2	0.74	10	0.0	End-point at Au_2N_3; yellow ppt.
		i 4.00 h	0.0015	0.2	0.49	20	0.0	End-point at Au_1N_1; white ppt.
279		i 3.9 h	0.0015	0.0	0.47	20	2.5	End-point at Au_1N_1; white ppt.
279		i 4.0 h	0.0015	0.2	0.50	15	0.0	End-point at Au_1N_1
	0.781	i.c. 3.00 h	0.002	0.0	0.55	14	0.0	End-point at Au_1N_1; yellowish ppt.
426	0.781	i 3.0 h	0.002	0.0	0.57	12	0.0	End-point at Au_1N_1
320*		i 4.20 h	0.002	0.4	0.82	8	1.2	End-point at $Au_1N_1 + Pd_2N_3$; pink ppt.
320*		c 4.20 h	0.002	0.4	0.85	7	1.2	End-point at $Au_1N_1 + Pd_2N_3$; pink ppt.
	0.781*	i 3.50 h	0.002	0.4	0.65	10	0.0	End-point at $Au_1N_1 + Pt_4N_3$; yellow ppt.
	0.781*	i 3.50 h	0.002	0.2	0.65	5	0.0	End-point at $Au_1N_1 + Pt_4N_3$
	0.781	i 4.40 h	0.002	0.0	0.76	5	2.2	End-point at $Au_1N_1 + Pt_4N_3$; lemon yellow ppt.
279	1.562*	c 4.0 h	0.0015	0.4	0.41	12	0.0	End-point at Pt_4N_3; brown ppt.
279	1.562*	c 4.0 h	0.0015	0.2	0.59	9	0.0	End-point at Pt_4N_3; yellow ppt.
426*	0.781*	c 4.50 h	0.002	0.2	0.90	10	0.0	End-point at $Pd_2N_3 + Pt_4N_3$
426*	0.781*	i 4.40 h	0.002	0.2	0.95	8	2.0	End-point at $Pd_2N_3 + Pt_4N_3$
426	1.562*	i 3.00 h	0.002	0.4	0.61	7	0.0	End-point at Pt_4N_3
067	1.562*	i 3.00 h	0.002	0.2	0.64	7	0.0	End-point Pt_4N_3; bright yellow ppt.
426	1.562*	i 3.00 h	0.002	0.6	0.54	9	0.0	End-point Pt_4N_3; bright yellow ppt.
	1.172	i 3.98 h	0.0015	0.2	0.52	13	0.2	End-point at Au_1N_1; yellow ptt.
067	0.781	i 4.00 h	0.0015	0.0	0.58	15	0.0	End-point at Au_1N_1; white ppt.
067	0.781	i 4.00 h	0.002	0.2	0.71	11	0.0	End-point at Au_1N_1; lemon yellow ppt.

ensity line.

Gold + palladium. In the presence of *dilute ammonia* and excesses of Na_3-citrate (Expts. 58) a white precipitate was obtained and only the gold was titrated as $Au_1N_1\downarrow\downarrow$. In the presence of *concentrated ammonia*, the palladium remained dissolved while the gold alone was determined as $Au_2N_3\downarrow\downarrow$ (Expt. 55) just as in the absence of palladium (*cf.* Table II, Expt. 39). The maximum density value was high and therefore this procedure can be especially recommended. It was very interesting to establish that when an excess of Na_2-EDTA was added to the solution together with the concentrated ammonia, the maximum density value was lower than before and only the gold was determined as $Au_1N_1\downarrow\downarrow$ (Expt. 57). (The lower density could also be caused by the presence of excesses of palladium.)

In contrast to this, the sum of gold and palladium, as $Au_1N_1 + Pd_2N_3\downarrow\downarrow$ was always obtained when ammonia was absent and complexing agents such as citrate or Na_2-EDTA were present (Expts. 61 and 62).

Gold + platinum. When concentrated ammonia was added only the gold was determined as $Au_1N_1\downarrow\downarrow$ (Expt. 73). The same result was obtained when in addition to the concentrated ammonia Na_2-EDTA was present. Here too the gold was determined solely as $Au_1N_1\downarrow\downarrow$ (Expt. 59). In the *absence of ammonia* but in the presence of excesses of a complexing agent, such as Na_3-citrate or Na_2-EDTA, the *sum* of both metals was obtained at the first maximum point as $Au_1N_1 + Pt_4N_3\downarrow\downarrow$ (Expts. 63 and 64).

Gold + palladium + platinum. Only the gold was determined as Au_1N_1 while the platinum and palladium were masked when the solution being analysed contained concentrated ammonia + Na_2-EDTA (Expts. 60 and 74).

Titrations of solutions of palladium chloride

Compounds

Using nitron as titrant, only one end-point was obtained in all cases at the point of the quantitative formation of $Pd_2N_3\downarrow\downarrow$. In reverse titrations using palladium chloride as titrant other compounds were obtained, amongst them the compound $Pd_1N_3\downarrow\downarrow$. No visible reaction whatsoever occurred between nitron and palladium chloride in the absence of potassium thiocyanate.

In the absence of other metals

Table I and Fig. 1 present a selection of such experiments, as well as the results obtained. Here too 1 ml $2M$ KCNS was entirely sufficient for a successful titration (Expts. 1 and 2) which lasted 5–10 minutes. However, when the solution contained very small amounts of *potassium thiocyanate* (Expt. 17) the density at the intersection point was lower and the density line showed a linear rise. 0.43 mg palladium (in 20 ml solution) was, in all cases, entirely sufficient for the analysis. The maximum density values were high (0.6 to 0.85) so that half the amount of palladium can, perhaps, still be analysed. The titrated solution may have a pH of $\sim$ 1–3 or $\sim$ 7–9 (Expts. 3, 4, 6, 7 and 8). The end-point was determined in all cases with equal accuracy. *Na_3-citrate* or *Na_2-tartrate* could be present in large excesses (Expts. 9–11). Even excesses of *tripolyphosphate* or *Na_2-EDTA* (Expts. 12 and 13) were without influence. In all cases a bright brown powder was obtained and the error was always near zero or less than 1%. Just as in the case of gold, no precipitation occurred in the presence of potassium cyanide (Expt. 15). No precipitation what all occurred when the solution contained *dilute ammonia* (Expt. 18) or excesses of Na_4-EDTA (Expt. 14). The compound Pd_2N_3 dissolved in 50% alcoholic solution (Expt. 16). The titration was normal even in a solution which contained a considerable amount of *ammonium nitrate* (conc. = $0.2M$) (Expt. 19).

In mixtures

Palladium + gold. Palladium could be determined only from the *sum* of both metals (Table IV, Expts. 61 and 62), as $Au_1N_1 + Pd_2N_3\downarrow\downarrow$.

Palladium + platinum. In this case also, the *sum* of both metals, as $Pd_2N_3 + Pt_4N_3\downarrow\downarrow$, was obtained at the end-point. The solution contained either no complexing agents at all (Expt. 68), or Na_2-EDTA in excess (Expt. 69). In the presence of even dilute *ammonia*, the palladium remained dissolved (Expts. 58, 66, 67, 70, 71 and 72); it could be determined in all cases by difference.

Titrations of solutions of chloroplatinic acid

Compounds

No visible reaction occurred between platinum and nitron in the absence of potassium thiocyanate. The composition of the compound, which was always obtained quantitatively when titrating chloroplatinic acid solution (containing potassium thiocyanate) with nitron was: $Pt_4N_3\downarrow\downarrow$. In reverse titrations, using the platinum solution as titrant, no precipitation occurred at pH's 7–9, while at lower pH's a compound $Pt_1N_3\downarrow\downarrow$ was obtained.

In the absence of other metals

The results are given in Table III. The platinum(IV) amounted in most cases to 1.562 mg, but in individual cases 0.78 mg was sufficient. The maximum density value was in the last case approximately equal to half the previous value. The presence of large excesses of potassium thiocyanate was not disadvantageous (Expts. 41 and 42). The compound Pt_4N_3 precipitated as a fine yellow powder.

From the experiments listed in Table IV it can be seen that no precipitation of platinum occurred in solutions containing more concentrated ammonia (0.5 ml conc. NH_3). But when the ammonia was diluted (Expt. 53) a regular precipitation of $Pt_4N_3\downarrow\downarrow$ occurred. The same compound was obtained quantitatively at pH's 1–9 in the presence and in the absence of complexing agents (Expts. 46, 47, 49, 50 and 51). Here also, no precipitation occurred in the presence of potassium cyanide (Expt. 52). In the presence of Na_4-EDTA a precipitate was formed, but the intersection point was not clear (Expt. 48). In all normal titrations the titration time was 5–10 minutes, and the error was less than 1%.

In mixtures

The experiments are presented in Table IV.

Platinum + palladium. It was easy to determine platinum alone in mixtures of platinum with palladium (Expts. 66, 67, 70, 71 and 72), by adding 1 ml M NH_3. The end-point always lay at the quantitative formation of $Pt_4N_3\downarrow\downarrow$. When *no complexing agent* at all was present, or when *Na_2-EDTA* was added in excess, the *sum* of both metals was measured as $Pt_4N_3 + Pd_2N_3\downarrow\downarrow$ (Expts. 68 and 69).

Platinum + gold. Only the sum of both metals could be determined as $Pt_4N_3 + Au_1N_1\downarrow\downarrow$; this could be carried out in solutions containing large excesses of Na_3-citrate or Na_2-EDTA (Expts. 63 and 64). But when the solution contained *concentrated ammonia* together with Na_2-EDTA (Expt. 59) or even concentrated ammonia alone (Expt. 73), the platinum remained dissolved and could be determined from the difference of two titrations.

ANALYTICAL ASPECTS

Gold(III), palladium(II) or platinum(IV) can be easily determined with precision within 10 minutes by a heterometric titration of the metal chloride in thiocyanate

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solution, with nitron. This solution may contain hydrochloric, nitric, acetic or phosphoric acid. The pH may be between 1 and 7. The solution may contain, in addition to the above, the following masking agents in excess: citrate, tartrate, Na_2-EDTA, pyro- or tripolyphosphate. The amounts of metal necessary for the analysis are: $\sim$ 0.5 mg palladium, $\sim$ 1 mg gold and $\sim$ 1.5 mg platinum. No filter is required. The error is always between zero and 1%. The end-point is always obtained from the intersection point of the following two lines: a line drawn through the optical density points of the last part of the titration curve (approximately the last quarter) and a line drawn through the horizontal density points *after* the end-point. In exceptional cases, the end-point is obtained from the contact point of the horizontal density line with the titration density curve.

In the case of gold, the sensitivity becomes somewhat higher (and the end-point is at $Au_2N_3\downarrow\downarrow$), when the heterometric titration is carried out in a solution that contains large excesses of ammonia (conc. $\sim$ 0.3*M*).

Composition of the compounds

The following compounds are quantitatively obtained at the end-point of the titration:

$$Au_1N_1\downarrow\downarrow;\ (Au_2N_3\downarrow\downarrow);\ Pd_2N_3\downarrow\downarrow;\ Pt_4N_3\downarrow\downarrow.$$

In strong ammoniacal solution the gold is precipitated as $Au_2N_3\downarrow\downarrow$. The structures of these and other compounds obtained will be discussed in a special report.

METHODS

Determination of gold

In the absence of other metals

I. (*as* Au_1N_1). 20 ml aqueous solution of gold chloride, which contains 1–1.5 mg gold, 1 ml 2*M* KCNS and may contain supplements, are titrated with 0.002*M*–0.0015*M* nitron.

Remark. The solution being analysed may contain the following supplements: 1 ml *M* HCl, 1 ml *M* HNO_3, 1–2 ml *M* CH_3COOH, 1 ml *M* H_3PO_4, 1 ml *M* Na-acetate, 1 ml *M* Na_3-citrate, 1 ml *M* Na_2-tartrate, 3 ml 0.2*M* Na_2-EDTA.

II. (*as* Au_2N_3). 20 ml aqueous solution of gold chloride, which contains $\sim$1 mg gold, 1 ml 2*M* KCNS and 0.5 ml conc. NH_3 are titrated with 0.002*M*–0.0015*M* nitron.

In mixtures of gold and palladium

III. (*as* Au_1N_1). 20 ml aqueous solution of gold chloride + palladium chloride, which contains $\sim$1 mg gold, 1 ml 2*M* KCNS and $\sim$1 ml *M* NH_3 are titrated with 0.002*M*–0.0015*M* nitron.

IV. (*as* Au_2N_3). As III, but the solution contains 0.5 ml conc. NH_3.

Remark. In both cases the palladium is masked by the ammonia. When the solution contains excesses of Na_2-EDTA in addition to the concentrated ammonia, the compound $Au_1N_1\downarrow\downarrow$ is obtained.

In mixtures of gold and platinum

V. (*as* Au_1N_1). 20 ml aqueous solution of gold chloride + chloroplatinic acid, which contains 1 ml 2*M* KCNS, $\sim$1 mg gold and 0.5 ml conc. ammonia are titrated with 0.002*M* nitron.

In mixtures of gold, palladium and platinum

VI. (*as* Au_1N_1). 20 ml aqueous solution of all three metals as chlorides, which contains $\sim$1 mg gold, 1 ml 2*M* KCNS, 0.5 ml conc. ammonia and 3 ml 2*M* Na_2-EDTA are titrated with 0.002*M*–0.0015*M* nitron.

Determination of palladium

In the absence of other metals

VII. (*as* Pd_2N_3). 20 ml aqueous solution of palladium chloride, which contains $\leqslant$ 0.5 mg palladium, 1 ml 2*M* KCNS and may contain supplements, are titrated with 0.0015*M* nitron.

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Remark. The solution being analysed may contain the following supplements: 1 ml M HCl, 1 ml M HNO_3, 1–2 ml M CH_3COOH, 1 ml M H_3PO_4, 1 ml M Na-acetate, 1 ml M Na_3-citrate, 1 ml M Na_2-tartrate, 3 ml 0.2M Na_2-EDTA.

Determination of platinum

In the absence of other metals

VIII. (*as* Pt_4N_3). 20 ml aqueous solution of chloroplatinic acid which contains $\sim$1.5 mg platinum, 1 or more ml 2M KCNS and may contain supplements, are titrated with 0.002M nitron.

Remark. The same supplements may be present as in (I).

In mixtures of platinum and palladium

IX. (*as* Pt_4N_3). 20 ml aqueous solution of platinum chloride + palladium chloride, which contains $\sim$1.5 mg platinum, 1 or more ml 2M KCNS, 1 ml M NH_3 and 1–2ml Na_3-citrate are titrated with 0.0015M nitron.

Determination of the sum of two or three metals

X. (*as* $Au_1N_1 + Pd_2N_3 + Pt_4N_3$). 20 ml solution which contains 1–2 mg of the metals, 1 ml 2M KCNS and 3 ml 0.2M Na_2-EDTA or 1–2 ml Na_3-citrate are titrated with 0.002M nitron.

SUMMARY

Methods are presented for a rapid and precise determination of gold(III), palladium or platinum(IV) either alone or in mixtures. The heterometric titrations were carried out in thiocyanate solutions with nitron. $\sim$1 mg gold, $\leqslant$ 0.5 mg palladium or $\sim$1.5 mg platinum (dissolved in 20 ml aqueous solution) were necessary for a determination, which lasted 5–10 minutes. The error was mostly between zero and 1%.

The insoluble compounds, which were quantitatively obtained at the end-points of the titrations, had the following compositions:

Au_1N_1; (Au_2N_3); Pd_2N_3 and Pt_4N_3. (N = nitron)

At pH 1–7 all these compounds were entirely insensitive to common masking agents, such as citrate, tartrate, ethylenediaminetetraacetate, pyro- and tripolyphosphate.

RÉSUMÉ

Des méthodes rapides et précises sont proposées pour le dosage de l'or, du palladium et du platine. Les titrages hétérométriques sont effectués en solutions thiocyaniques, au moyen de nitron. Les composés insolubles obtenus aux points finals des titrages sont les suivants: Au_1N_1; (Au_2N_3); Pd_2N_3 et Pt_4N_3 (N = nitron).

ZUSAMMENFASSUNG

Es werden rasche und genaue Methoden für die Bestimmung von Gold, Palladium und Platin vorgeschlagen. Die heterometrischen Titrationen werden in Thiocyanatlösung mit Nitron vorgenommen. Die beim Endpunkt der Titrationen erhaltenen unlöslichen Verbindungen haben folgende Zusammensetzungen: Au_1N_1; (Au_2N_3); Pd_2N_3 und Pt_4N_3 (N = Nitron).

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PHOTOMETRIC TITRATION OF IRON WITH ETHYLENEDIAMINEDI(*o*-HYDROXYPHENYLACETIC ACID)

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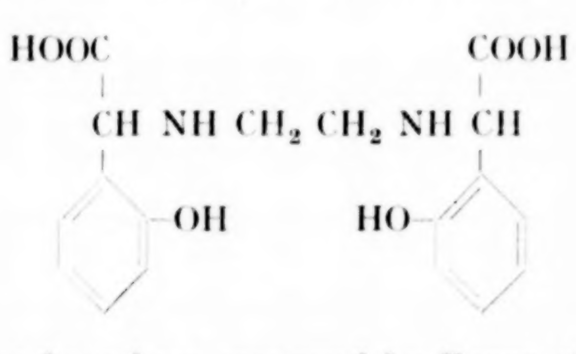
The synthesis of ethylenediaminedi(*o*-hydroxyphenylacetic acid) or N,N'-ethylenebis[2-(*o*-hydroxyphenyl)-glycine], a compound analogous to ethylenediaminetetraacetic acid, was reported recently by KROLL *et al.*[1]. Stability constants of a few of its metal chelates have been measured by FROST *et al.*[2], and a spectrophotometric method for determining iron in concentrations below about 10 p.p.m. has been described by UNDERWOOD[3], based upon the very stable, red ferric chelate. This new reagent is interesting because it possesses some of the attributes of ethylenediaminetetraacetic acid while it also bears chromophoric groups not found in EDTA. It is too early to predict what ultimate utility it will find as an analytical reagent; in the meantime, like all interesting reagents, it should be tested in a variety of situations. In this paper, it is shown that ferric iron in fractional mg amounts (or μg-amounts by scaling down the procedure) can be titrated with ethylenediaminedi(*o*-hydroxyphenylacetic acid), making use of a photometric end-point. Because only absorbance changes rather than absolute absorbance values are needed to fix such an end-point, certain interferences in an ordinary spectrophotometric method might be circumvented by the titration technique. The end-point should, moreover, be more accurate than isolated absorbance measurements. Further general information about photometric titrations may be found in the literature[4,5].



EXPERIMENTAL

Apparatus and reagents

Photometric titrations were performed using a Beckman Model DU spectrophotometer adapted as described previously[6]. The length of the light path through the titration cell was 1.7 cm. The titrant was delivered from a 10-ml buret graduated in 0.02-ml units. pH values were measured with a Beckman Zeromatic pH meter.

A standard ferric solution was prepared by dissolving 1.000 g of pure iron wire in 20 ml of 1:1 nitric acid, boiling the solution for a few minutes, and diluting to exactly 1 l with distilled water. Dilutions of this stock solution were prepared as required, with the addition of sufficient nitric acid to prevent hydrolysis of the iron.

As noted below, most of the titrations were performed at pH 3.5. Solutions were buffered at this pH value with a 1M chloroacetate buffer prepared by dissolving 48 g of monochloroacetic acid in 400 ml of distilled water, adjusting the pH to 3.5 by the addition of concentrated sodium hydroxide solution, and diluting the solution to 500 ml.

The reagent ethylenediaminedi(*o*-hydroxyphenylacetic acid) was obtained from the Geigy Industrial Chemicals Division of the Geigy Chemical Corporation, Ardsley, N.Y., under the trade name of Chel 138. As noted before[3], the reagent contains dark-colored impurities which probably result from air oxidation of the phenolic portions of the molecule. It was purified for this work by suspending it in water, adding the minimal amount of sodium hydroxide to effect solution, treating the solution with charcoal, and acidifying to pH 4 with hydrochloric acid. The white precipitate was washed with water and dried in a vacuum desiccator over silica gel. It remains white indefinitely when kept dry. A 0.01M solution of the reagent was prepared by suspending 2 g of the solid in 400 ml of water, slowly adding just enough sodium hydroxide to effect solution (the pH of the solution was about 8.8 at this point), and diluting to 500 ml with water. The solution was treated with charcoal to remove a small trace of colored material and filtered into a reagent bottle. Oxygen-free nitrogen was bubbled through the solution for about 30 min, and the bottle was tightly closed. The iron titer of this solution remained undiminished throughout daily checks over a period of 3 weeks.

Effect of pH

In developing the spectrophotometric method for iron using ethylenediaminedi(*o*-hydroxyphenylacetic acid), it was shown[3] that color development was maximal throughout the pH range of 2.5 to 9.5. However, excess reagent was used, whereas a sharp photometric end-point requires that the chelation reaction go well toward completion with quantities of reagent more nearly stoichiometric. The effect of pH on the titration is shown in Fig. 1, where it may be seen that the pH should be at least 3 in order to obtain a reasonably good titration curve. The titrations shown in the figure were set up by adding 10 ml of the chloroacetate buffer to a solution con-

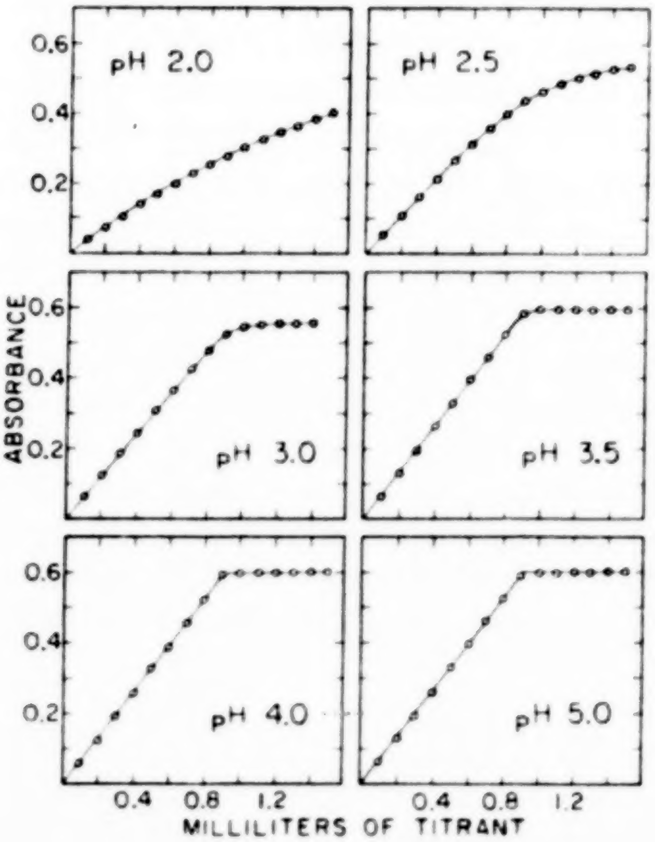


Fig. 1. Effect of pH.

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taining 0.5 mg of ferric iron, diluting to about 100 ml, and adjusting the pH to the desired value with drops of concentrated hydrochloric acid or sodium hydroxide solutions. (For pH values greater than 3.5, an acetate buffer was substituted for the chloroacetate.) As a compromise between staying on the safe side of the lower pH limit and retaining a pH as low as possible, all further titrations were performed at pH 3.5.

Reproducibility

Table I shows the results of a number of titrations involving small quantities of ferric iron in pure solution. 15 samples ranging from 0.2 to 1 mg show an average deviation of 5.5 μg, or about 1%. The volume in all cases was about 100 ml, so that the ferric concentrations titrated ranged from about $3.6 \cdot 10^{-5}$ to $1.8 \cdot 10^{-4}$ *M*. The reproducibility is satisfying in this context. The results shown in the table include all of those obtained in a certain day's work; results from day to day are about the same. Certain statistical tests would permit one to discard a few of the results, leading to a much better apparent reproducibility. The end-points in the titrations are found by graphical extrapolation from a few points taken before and after the end-point. It is important to plot the data in such a way that the graphical process itself does not limit the reproducibility. This has been emphasized by GODDU AND HUME[4].

TABLE I

TYPICAL RESULTS

Iron taken mg	*Iron found* mg	*Deviation* mg	*Deviation* %
0.2000	0.2043	0.0043	2.2
0.2000	0.2043	0.0043	2.2
0.3000	0.3078	0.0078	2.6
0.4000	0.4001	0.0001	0.0
0.4000	0.4029	0.0029	0.7
0.5000	0.4980	0.0020	0.4
0.5000	0.4897	0.0103	2.1
0.5000	0.4980	0.0020	0.4
0.6000	0.6044	0.0044	0.7
0.6000	0.6016	0.0016	0.3
0.7000	0.6939	0.0061	0.9
0.8000	0.7890	0.0110	1.4
1.0000	0.9961	0.0039	0.4
1.0000	0.9849	0.0151	1.5
1.0000	0.9933	0.0067	0.7

Average deviation: 0.0055 mg.

Iron concentration range

With the particular cell used for these titrations, 0.8 mg of iron in a volume of 100 ml leads to an absorbance value of about 1 at the end of the titration when the wave length is 470 mμ, the absorption maximum for the red ferric chelate[3]. To titrate larger quantities of iron, it is desirable to change to a wave length where lower sensitivity obtains. This flexibility, indeed, is one of the attractive features of photometric titrations. 2 mg of iron in a volume of 100 ml led to an ultimate absorbance of about 0.95 at a wave length of 550 mμ. A series of titrations in this concentration range displayed an average deviation of about 0.6%. The larger volume of titrant may partly account for this improvement over the results shown in Table I for lesser quantities of iron.

Since a volume of 100 ml is not obligatory, much smaller quantities of iron can be titrated easily by scaling down the procedure. It is advisable then to employ a more dilute titrant so that the buret readings are sufficiently precise. For example, 0.1 mg of iron in 50 ml of solution is nicely titrated with 0.001 M reagent with errors of less than 1%.

Effect of other metals

In a series of titrations of 0.5 mg of iron in 100 ml, 50-mg quantities of fourteen other metal ions were tested for interference. The following ions did not affect the titration in any way: magnesium, calcium, chromium(III), manganese(II), cobalt(II), zinc, cadmium, mercury(II), and lead. Thorium formed a precipitate when the solution was adjusted to pH 3.5 before the titration was started. Silver likewise formed a precipitate when the buffer was added, perhaps because of the presence of chloride in the chloroacetate solution. Aluminum caused slightly high results. With nickel, the results were correct but the titration took slightly more time than usual because of a drift in the absorbance values following each increment of titrant. In the case of copper, the drift was so persistent that the titration was considered non-feasible. Apparently a question of kinetics is involved: the titrant reacts with copper locally near the buret tip, and the shift to the more stable ferric chelate occurs very slowly after the solution has been mixed.

DISCUSSION

The titration of very dilute ferric iron solutions with the reagent ethylenediaminedi(*o*-hydroxyphenylacetic acid) using a photometric end-point works very well. A number of other metals do not interfere. The photometric titration can be performed easily and rapidly, employing a simple adaptation of ordinary spectrophotometric apparatus. It would be overly optimistic to envision wide general acceptance of this titration for determining iron, but one can easily imagine that it may be very useful in certain applications where particular interference problems must be circumvented.

SUMMARY

Fractional mg quantities of ferric iron in 100 ml of solution can be titrated at pH 3.5 with a solution of ethylenediaminedi(*o*-hydroxyphenylacetic acid). The end-point is found photometrically. Errors are generally under 1%, and a number of metals do not interfere. By scaling down the volume of the solution and the titrant concentration, the titration can be extended to μg quantities of iron, and mg quantities are also accessible by changing to a wave length where the sensitivity is not so great. The titration may be useful in certain applications.

RÉSUMÉ

Le fer(III) peut être titré par une solution d'acide éthylènediamine di(*o*-hydroxy-phénylacétique). Le point final est déterminé photométriquement. Les erreurs sont généralement inférieures à 1%. Plusiers métaux ne gênent pas.

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ZUSAMMENFASSUNG

Eisen-(3) kann mit einer Lösung von Äthylendiamin-di-(*o*-hydroxyphenylessigsäure) titriert werden. Der Endpunkt wird photometrisch bestimmt. Die Fehler liegen meistens unter 1%. Eine Reihe von Metallen zeigt keine Störung der Titration.

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U.V. ABSORPTION SPECTRA OF 8-OXYQUINOLINE AND ITS COPPER CHELATE

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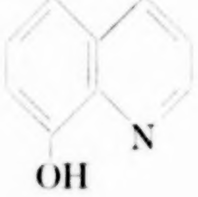
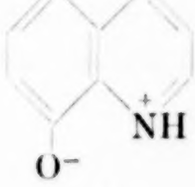
A comparative study of the absorption spectra of an organic ligand and its metal chelate can provide useful information regarding the nature of binding of the metal atom in the chelate. This has been shown by Basu and Chatterjee[1,2] for chelates of acetyl acetone and quinoline 8-carboxylic acid. In the present communication the same method has been applied to secure information regarding the structure of the copper complex of 8-oxyquinoline.

In solution, 8-oxyquinoline should exist as I; despite the presence of the basic N atom in the molecule a zwitterion structure II is less probable in view of the weakly acidic character of the phenolic group.

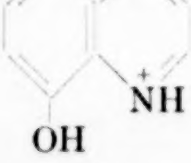


I

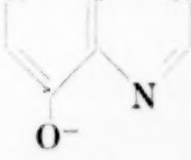


II

In acidic and alkaline media the molecule in all probability acquires the structures III and IV respectively.



III



IV

In 95% ethyl alcoholic solution the free ligand has two absorption maxima at 242 mμ and 310 mμ (Fig. 1). In 0.1*N* KOH in 95% alcohol, the band at 242 mμ shifts to 256 mμ. The second band is broad and diffuse and may be looked upon as made up of two overlapping bands with maxima at 340 mμ and 370 mμ respectively (Fig. 1). In 0.1*N* perchloric acid the ligand band shows absorption maxima at 255 mμ, 310 mμ, 320 mμ and 370 mμ (Fig. 2). The copper chelate of 8-oxyquinoline shows two absorption maxima at 258 mμ and 395 mμ respectively (Fig. 2). The nature of the absorption curve is similar to that of the ligand itself but the 310-mμ ligand band is shifted to 395 mμ.

The chelate cannot be ionic, for the characteristic absorption band of the ligand in the alkaline medium is absent in the chelate. It cannot have a simple covalent structure (V) for this will put a positive charge on the N atom and the characteristic band of the ligand in the acid solution should be present in the chelate, while contrary is the case.

It is also important to account for the shift of the ligand absorption band at 310 mμ to 395 mμ in the chelate. Obviously this indicates a larger resonating path of the

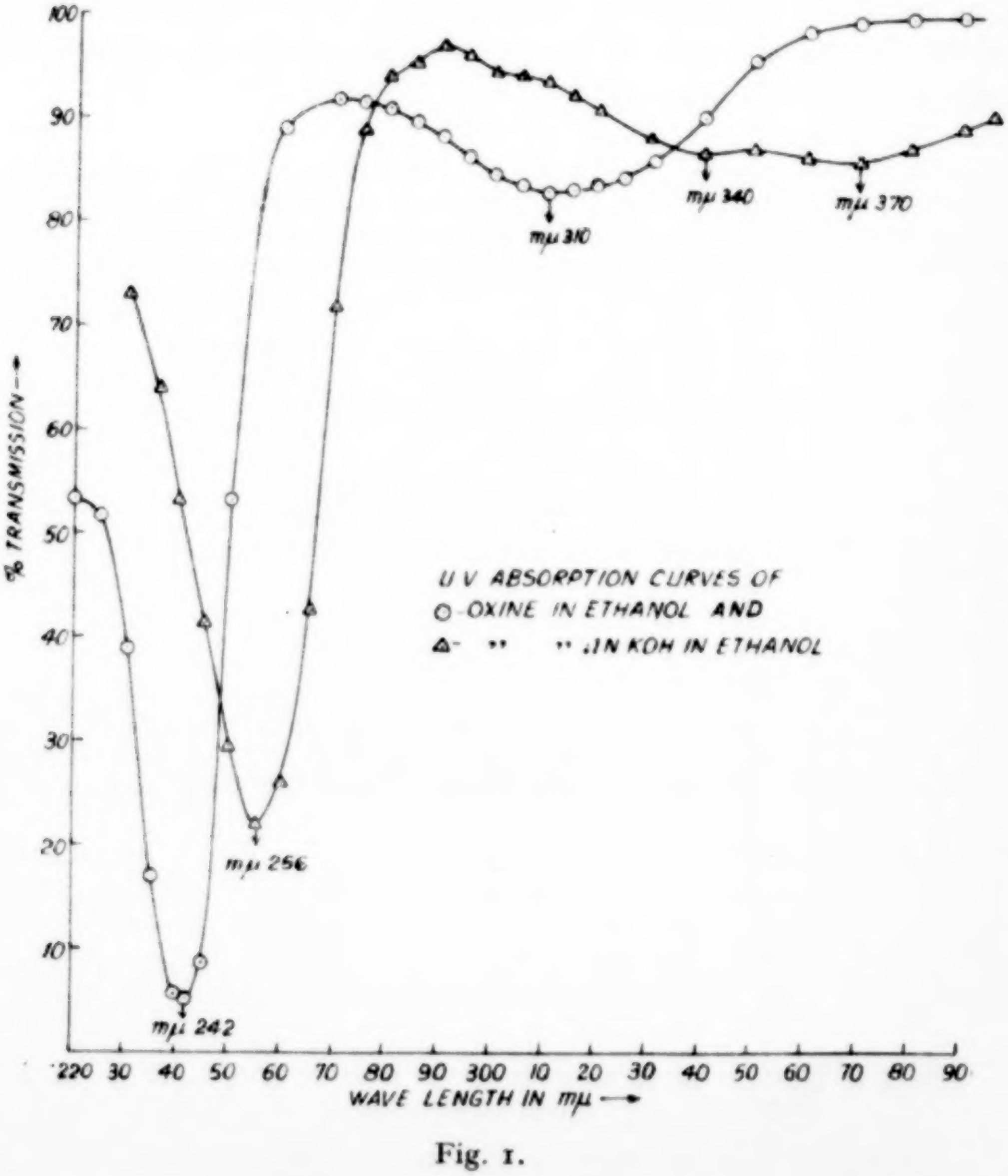
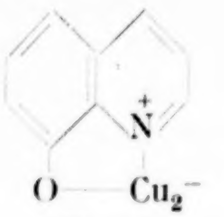
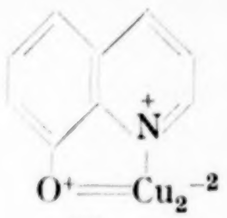


Fig. 1.

electrons in the chelate than in that of the ligand itself. All these characteristics can however be explained if the structure VI be accepted for the chelate.



V



VI

In this structure Cu is doubly bonded to oxygen and since the double bond is in conjugation with the double bonds in the ring system, the structure shows characteristic absorption of its own which we attribute to the 295-mμ band.

The structure, however, presupposes a planar configuration, in which copper is in dsp^2-hybridised state; the additional pπ–dπ bond possibly confers further stability to the planar structure.

MERRITT, CADY AND MUNDY[3] have cited X-ray evidence in favour of a tetrahedral configuration of anhydrous copper oxinate. The space group P $2_1/a$ reported by the last named authors apparently indicates that the molecule is non-centrosymmetric but this is not quite conclusive. Also an outer level sp^3-configuration for the copper complex should have considerable contribution from the ionic structure and the characteristic absorption band of the oxinate ion should be present in the chelate which is not actually the case.

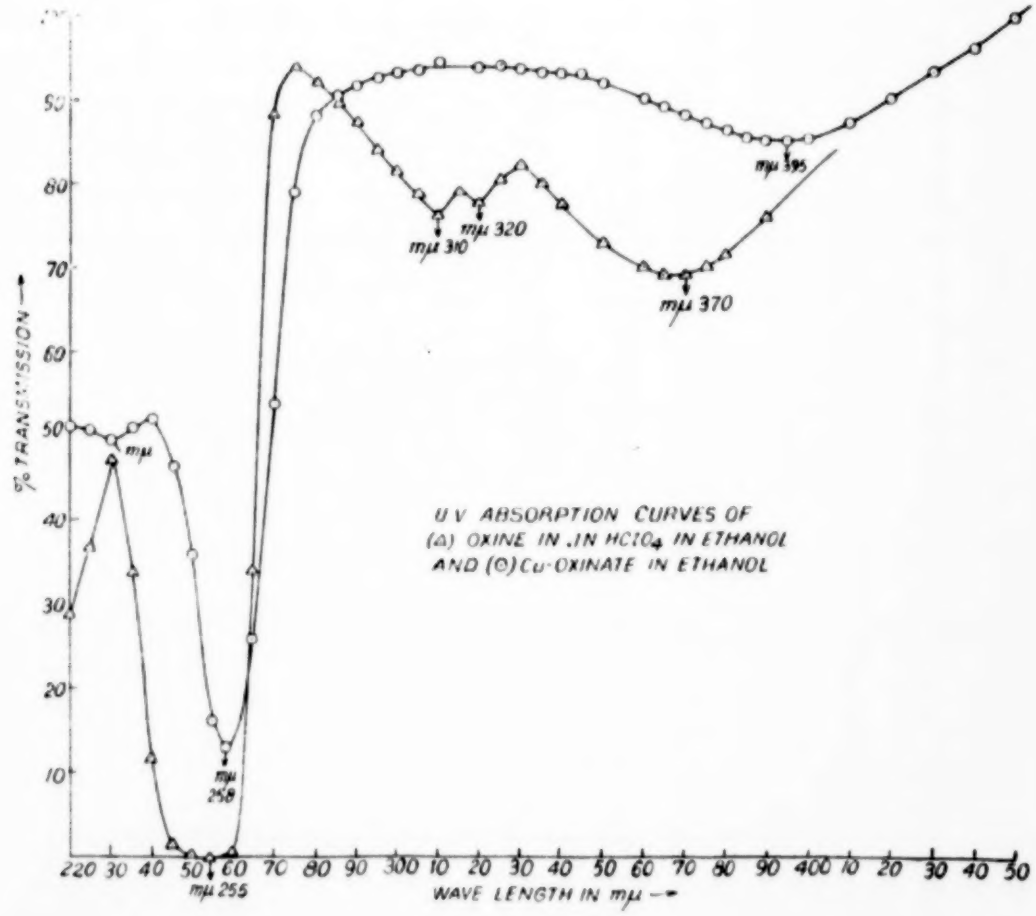


Fig. 2.

The structural analogy of zinc oxinate dihydrate and copper oxinate dihydrate as implied by the above workers is not tenable. In the zinc compound itself for which sp^3-d^2-configuration has been suggested there is considerable difference between the polar and equatorial Zn–O bond distances, indicating the non equivalence of these bonds. Such octahedral sp^3–d^2-structure for the hydrated copper complex will be still less probable, since in this case the water molecules are more loosely bound than that of the zinc complex. This is indicated by the fact that whereas the zinc compound loses water at 135°, the copper complex is completely dihydrated at 105°. Further, it has recently been shown by JONES *et al.*[4] that in all probability there is π-bonding between metal and ligand in nickel-8-oxyquinoline chelate, which evidently presupposes a planar structure for the chelate. The possibility for such a planar structure is even greater in copper chelates.

Ultraviolet absorption measurements were carried out with the help of Beckman model D.U. quartz spectrophotometer using 1-cm quartz absorption cells. The alcohol used was refluxed for 6–8 h with solid caustic soda and distilled. It showed complete transmission down to 220 mμ. The concentrations of the solutions employed were 10^{-4}–$10^{-5}M$.

ACKNOWLEDGEMENT

The author's best thanks are due to Dr. SADHAN BASU D.Sc. F.R.I.C. for his keen interest and helpful suggestions.

SUMMARY

From a comparison of the U.V. absorption spectra of the copper chelate of 8-oxyquinoline in ethyl alcoholic solution with those of the ligand itself in the same medium and in the presence of $0.1\,N$ $HClO_4$ and $0.1\,N$ NaOH respectively, a probable structure for the former has been suggested. The structure presupposes a planar configuration for the complex and a metal–ligand double bonding.

RÉSUMÉ

Une étude a été effectuée en vue de déterminer la structure probable du chélate cuivre-hydroxy-8-quinoléine.

ZUSAMMENFASSUNG

Es wird eine Untersuchung zur Ermittlung der wahrscheinlichen Struktur des Kupfer-8-oxychinolats beschrieben.

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THE USE OF NAPHTHALENE DERIVATIVES IN INORGANIC ANALYSIS

VII. THE NITRONAPHTHOLS AS FLUORIMETRIC REAGENTS FOR STANNOUS TIN

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INTRODUCTION

In earlier papers of this series, the use of naphthalene compounds has been reported for the fluorimetric detection of various cations[1-6]. In particular, nitronaphthalene derivatives have been utilized for the fluorimetric detection[1,3-6] and determination[7] of stannous tin. For this paper, the nitro derivatives of 1-naphthol and 2-naphthol have been examined and found to be of importance in the detection of tin by fluorimetric methods. Spots of aqueous solutions of 49 metal salts were placed on No. 1 Whatman Chromatographic paper, air dried and then sprayed separately with 0.1% solution of the reagents dissolved in a mixture of equal volumes of 96% ethyl alcohol and 10*N* hydrochloric acid. The paper was air dried, sprayed with 15*N* NH_4OH, again air dried and viewed under ultra-violet light. Under these conditions only stannous tin exhibited any marked fluorescence. The addition of 10*N* HCl to the alcoholic solutions of the nitronaphthols was found to increase the sensitivity of the test. The intensity of fluorescence was found to vary with the position of the nitro group in the naphthol nucleus.

EXPERIMENTAL

Synthesis of reagents

A summary of the methods of synthesis of the nitro-naphthols will be published in the near future by BRYSON[8]. All nitro-naphthols can be synthesized from the corresponding nitro-naphthylamines[4] by a diazotisation procedure and subsequent replacement of the diazo group by hydroxyl. The synthesis of 5-nitro-1-naphthol from 5-nitro-1-naphthylamine is an example of the procedure used for the preparation of the nitronaphthols.

5-Nitro-1-naphthol

5-Nitro-1-naphthylamine** (0.8 g) was warmed in a mixture of sulphuric acid (5 ml, sp.gr. – 1.84) and water (50 ml), then cooled to 0–5° so that the nitronaphthylamine was present in a finely divided state as the sulphate paste, the most suitable form for efficient diazotisation. A solution of sodium nitrite (0.5 g) in water (2.5 ml) was added from a dropping funnel over a period of 10 min at 0–5° and the presence of excess, nitrous acid confirmed by the starch–potassium iodide test. The mixture was stirred for 1 h at 0–5°, then urea (0.1 g) added to destroy excess nitrous acid. The diazo solution was now added slowly over a period of 10 min to 2*N* H_2SO_4 maintained just below the boiling point. After the addition was completed, the mixture was boiled for a further 10 min, filtered hot and the filtrate chilled. The flocculent yellow crystals of 5-nitro-1-naphthol were separated and recrystallised from boiling water using a trace of activated charcoal to remove the small amount of red dye which unavoidably forms during the sulphuric acid decomposition step.

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* On study leave at Birkbeck College, University of London.

** For the synthesis of this compound see GARNETT AND LOCK[4].

Yield 0.5 g; m.p. 171–2°; Literature 171°[8]

The same procedure was used for the synthesis of the remaining nitronaphthols, except 8-nitro-1-naphthol and 6-nitro-2-naphthol.

8-Nitro-1-naphthol

When the diazo compound from 8-nitro-1-naphthylamine was decomposed in 2*N* H_2SO_4, following the same procedure as previously reported, excessive coupling appeared to occur, resulting in bad tarring and a very poor yield (approx. 10%) of 8-nitro-1-naphthol. The yield was improved to 30% by using stronger sulphuric acid (4*N*) in the decomposition step. BRYSON[8] suggests that even better yields can be obtained if the diazonium solution is slowly added to the sulphuric acid at 50° (instead of 95°) and the solution slowly brought to the boil. This minimises the loss of 8-nitro-1-naphthol through the competing coupling reaction.

6-Nitro-2-naphthol

This compound can also be readily synthesized from the corresponding nitronaphthylamine by the diazotisation procedure[8], however the authors have used an alternative method of preparation which involves a pressure desulphonation of 6-nitro-2-hydroxy-naphthalene-8-sulphonic acid in 10*N* HCl.

A solution of 6-nitro-2-hydroxy-naphthalene-8-sulphonic acid* (1.0 g) in 10*N* HCl (10 ml) was carefully heated to 160° for 2 h in a sealed glass tube, then cooled. The solution was diluted with water (90 ml) and the precipitate filtered, dried and recrystallised from benzene in pale yellow needles.

Yield 0.48 g; m.p. 158–9°

This compound showed no depression of melting point when mixed with an authentic sample of 6-nitro-2-hydroxynaphthalene prepared from 6-nitro-2-naphthylamine by a diazotisation procedure.

The observed and reported melting points of the nitro-naphthols are listed in Table I and compared with those of the parent α- and β-naphthols.

TABLE I

MELTING POINTS OF THE NITRONAPHTHOLS

Substituent NO_2	*OH*	*Observed m.p.* °C	*Literature m.p.* °C
	1	95.5	96
	2	122	122
2	1	127.5	128
3	1	168–9	167–8
4	1	166	164
5	1	171–2	171
6	1	181–2	181–2
7	1	212[a]	—
8	1	242[d]	212[d]
1	2	103	103
4	2	120	120
5	2	148	147
6	2	159	156–8
7	2	163	159
8	2	145	145

[a] 7-Nitro-1-naphthol is a new compound, the synthesis of which will be described elsewhere[8].

[d] decomposed without melting.

It will be noticed that the observed and reported melting points for 8-nitro-1-naphthol do not agree. BRYSON[8] discusses this anomaly and presents strong evidence to support the observed melting point.

From Table I, it can be seen that 13 of the theoretically possible 14 nitro-naphthols

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* See ANDERSON, GARNETT AND LOCK[6] for the synthesis of this compound.

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are listed, 3-nitro-2-naphthol being the exception. This compound can be synthesized from 3-nitro-2-naphthylamine. However, this is the most difficult of all nitronaphthylamine preparations and was unavailable in sufficient quantity for the preparation of the corresponding nitronaphthol.

Technique of spot testing

The standard procedure reported in previous communications[1,3] was used. The reagents employed are listed in Table II. The results obtained are shown in Table III.

TABLE II

REAGENTS USED FOR SPRAYING METAL IONS

Reagent No.	*Reagent* *0.1% Solution in a mixture of equal volumes of 96% ethyl alcohol and 10N HCl*	*Reagent No.*	*Reagent* *0.1% Solution in a mixture of equal volumes of 96% ethyl alcohol and 10N HCl*
1	2-Nitro-1-naphthol	8	1-Nitro-2-naphthol
2	3-Nitro-1-naphthol	9	4-Nitro-2-naphthol
3	4-Nitro-1-naphthol	10	5-Nitro-2-naphthol
4	5-Nitro-1-naphthol	11	6-Nitro-2-naphthol
5	6-Nitro-1-naphthol		
6	7-Nitro-1-naphthol	12	7-Nitro-2-naphthol
7	8-Nitro-1-naphthol	13	8-Nitro-2-naphthol

TABLE III

FLUORESCENCE OBTAINED ON SPRAYING SPOTS OF IONS WITH VARIOUS REAGENTS, BEFORE (B) AND AFTER (A) QUENCHING WITH 15N NH_4OH

	Reagent																									
	1		*2*		*3*		*4*		*5*		*6*		*7*		*8*		*9*		*10*		*11*		*12*		*13*	
Ion	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A
Sn^{+2}	F(s)	F(s)	F	F	F	F	F	F	F(s)	F	F(s)	F	F(s)	F(h)	F(s)	F	F	F	F(s)	F	F(s)	F	F(s)	F(s)	F(s)	F
Sn^{+4}																			F(t)							
As^{+5}										F(t)																
Al^{+3}																			F(t)					F(t)		
Li^{+}																					F(t)					
Be^{+2}								F(t)		F(t)				F(t)				F(t)	F(t)	F(t)	F(t)	F(t)		F(t)		
Th^{+4}																			F(t)							
ZrO^{+2}										F(t)								F(t)	F(t)					F(t)	F(t)	
Ti^{+4}																								F(t)		
In^{+3}																				F(t)				F(t)		

Other ions tested included: Fe^{+2}, Fe^{+3}, Hg^{+}, Hg^{+2}, As^{+3}, Sb^{+3}, Bi^{+3}, Cr^{+3}, Mn^{+2}, Zn^{+2}, Sr^{+2}, Ca^{+2}, Ba^{+2}, Mg^{+2}, Cu^{+2}, Co^{+2}, Ni^{+2}, Pb^{+2}, Na^{+}, K^{+}, Rb^{+}, Cs^{+}, Ce^{+3}, Ce^{+4}, Mo^{+6}, Pt^{+2}, Pt^{+4}, Au^{+3}, Pd^{+2}, Tl^{+}, Tl^{+3}, W^{+6}, UO_2^{+2}, VO^{+2}, V^{+5}, Ru^{+3}, Ti^{+3}, Cd^{+2}, Ag^{+}.

These ions gave either no fluorescence or coloured spots with only a faint trace of fluorescence.

B = Before quenching with 15N NH_4OH
A = After quenching with 15N NH_4OH
F = Fluorescence
F(s) = Slight fluorescence
F(t) = Trace of fluorescence
F(h) = Coloured spot with faint fluorescent ring

Effect of acid upon the test

Two series of sensitivity tests were performed using (a) the nitronaphthols dissolved in 96% ethyl alcohol and (b) the nitronaphthols dissolved in equal volumes of 96% ethyl alcohol and 10*N* HCl. The results are summarised in Table IV.

TABLE IV

EFFECT OF ACID UPON THE INTENSITY OF FLUORESCENCE

Reagent	*Reaction with* Sn^{+2}		*Reagent*	*Reaction with* Sn^{+2}	
Series I 0.1% *in* 96% *ethyl alcohol*	*B*	*A*	*Series II* 0.1% *in equal volumes of* 96% *ethyl alcohol and* 10*N HCl*	*B*	*A*
2-Nitro-1-naphthol	WF	WF	2-Nitro-1-naphthol	WF	WF
3-Nitro-1-naphthol	F	F	3-Nitro-1-naphthol	F	SF
4-Nitro-1-naphthol	WF	F	4-Nitro-1-naphthol	F	F
5-Nitro-1-naphthol	WF	WF	5-Nitro-1-naphthol	F	F
6-Nitro-1-naphthol	WF	WF	6-Nitro-1-naphthol	WF	F
7-Nitro-1-naphthol	WF	F	7-Nitro-1-naphthol	WF	F
8-Nitro-1-naphthol	WF	F(h)	8-Nitro-1-naphthol	WF	F(h)
1-Nitro-2-naphthol	WF	WF	1-Nitro-2-naphthol	WF	F
4-Nitro-2-naphthol	F	F	4-Nitro-2-naphthol	F	SF
5-Nitro-2-naphthol	F	F	5-Nitro-2-naphthol	WF	SF
6-Nitro-2-naphthol	WF	WF	6-Nitro-2-naphthol	WF	F
7-Nitro-2-naphthol	WF	WF	7-Nitro-2-naphthol	WF	WF
8-Nitro-2-naphthol	WF	F	8-Nitro-2-naphthol	WF	SF

SF = Strong fluorescence
F = Fluorescence
WF = Weak fluorescence
F(h) = Coloured spot surrounded by a faint fluorescent ring
B = Before quenching with 15*N* NH_4OH
A = After quenching with 15*N* NH_4OH

The above results are in agreement with the data reported for the nitronaphthylamines[4] where the presence of strong hydrochloric acid in the reagent solution improved the fluorescent properties of the particular reagent in the detection of stannous tin.

Sensitivity tests

Sensitivity tests were carried out on freshly prepared dilute solutions of stannous chloride containing 2 ml of 30% hypophosphorous acid per 100 ml of solution[3]. All the nitronaphthols exhibited a blue fluorescence under the conditions of test except reagent No. 7 which yielded a purple spot with a fluorescent ring. Reagent Nos. 1, 8 and 12 gave only slight fluorescence. Reagent Nos. 2, 9, 10 and 13 gave the most intense fluorescence of the series and were capable of detecting 10^{-5} g stannous tin whilst the remaining reagents were sensitive to 10^{-4} g stannous tin. The nitro derivatives of 2-naphthol produced more intense fluorescence than the corresponding derivatives of 1-naphthol. Blank experiments were performed on the dilute hypophosphorous acid solutions described previously and were found to yield no fluorescence.

DISCUSSION

In earlier papers of this series, it has been shown that both the nitronaphthylamines[4] and nitro-aminonaphthalene monosulphonic acids[1,3,5] can be used as fluorimetric reagents for stannous tin, the species responsible for the fluorescence being the excited state of the naphthylammonium ion. More recent evidence indicates that the test will also be given by other nitronaphthalene derivatives, in particular 6-nitro-2-hydroxy-naphthalene-8-sulphonic acid[5] and the reagents reported in this paper, the nitro-naphthols.

In general, the trend of the results with the nitronaphthols confirms the earlier work reported for the nitronaphthylamines, bearing in mind that the nature of the tests enables only a semi-quantitative study to be made of the type and intensity of the fluorescence exhibited by each compound.

From evidence available at present, the following conclusions can be made when attempting to correlate the effect of structure of reagent with intensity of fluorescence.

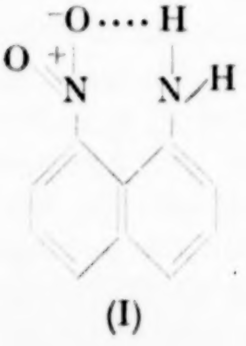
(1) Those substituted naphthalene derivatives (either naphthylamines or naphthols) containing a nitro group in the second ring appear to yield a more intense fluorescence than the corresponding homonuclear substituted nitro compounds.

(2) The nitro derivatives of the β-substituted naphthalenes (naphthylamines or naphthols) produce a more intense fluorescence than the corresponding nitro derivatives of the α-substituted compounds.

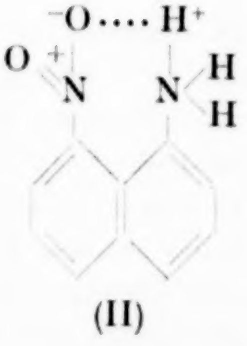
These results are in agreement with the data reported by ALLEN and his co-workers[9] who studied the effect of substituents in the naphthalene ring upon the fluorescent properties of the individual compounds, also the results of TOMASCHEK[10] who reports that the presence of substituents —OH and —NH_2 intensify the fluorescence of a particular compound and displace it towards the longer wavelengths.

The exceptions to the above conclusions are the 8-nitro-1-substituted naphthalene derivatives which exhibit poor reactivity in the stannous tin test when compared with the remaining isomers of each particular series. Both 8-nitro-1-naphthylamine[4] and 8-nitro-1-naphthol, in either weakly or strongly hydrochloric acid solution yield poor fluorescence with stannous tin. It is suggested that hydrogen bonding is responsible for this phenomenon *i.e.* the ease of reduction of the nitro group is impaired by a hydrogen bond to, either the amino group in the case of 8-nitro-1-naphthylamine[4], or to the hydroxyl group in the case of 8-nitro-1-naphthol. This hydrogen bonding will be exhibited by both the free base and the acidic forms of the compounds as figures (I, II and III) illustrate.

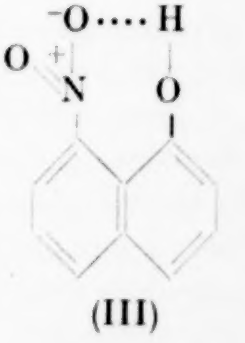
E.g.



(I)



(II)



(III)

Further support for the presence of an intramolecular hydrogen bond in these compounds is shown by the relatively poor reactivity already observed when 8-nitro-1-naphthylamine[4] is diazotised and the diazonium group replaced by hydroxyl. 8-Nitro-1-naphthylamine[4] exhibits the least reactivity of the nitronaphthylamine series in this reaction and the slow rate of diazotisation may be attributed to the existence of a hydrogen bond between the nitro and amino groups.

In the *ortho*-substituted compounds (*i.e.* 2-nitro-1- and 1-nitro-2-derivatives) this same lack of reactivity is not as appreciable as with the 8-nitro-1-compounds. Both *ortho* derivatives are readily diazotised and yield a positive stannous tin test, although the fluorescence is not so intense as with the remaining isomers of the series (except for the 8-1 derivative). Obviously the hydrogen bonding in the *ortho* derivatives (IV, V) does not influence the ease of reduction of the compounds as markedly as the hydrogen bonding does in the 8-1 derivative.

This observation is consistent with the effect of *ortho* nitro substituents on the acidity of phenols and anilinium ions[11]. With these systems, it is found that such factors do not appreciably affect the basic strength except in N-substituted anilines. Some indication of this effect can be seen from an analysis of Table V[11].

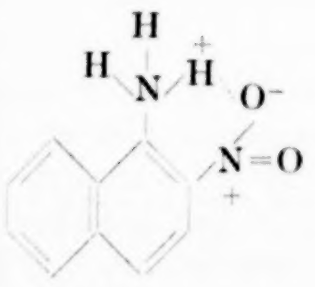
TABLE V

IONIZATION CONSTANTS OF SOME PHENOLS IN WATER SOLUTION

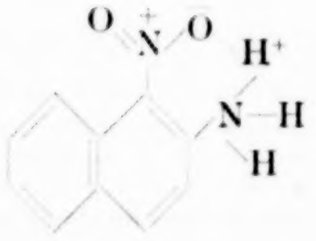
Compound	*K*
Phenol	$1.2 \cdot 10^{-10}$
o-Nitrophenol	$6.8 \cdot 10^{-8}$
m-Nitrophenol	$5.0 \cdot 10^{-9}$
p-Nitrophenol	$7.0 \cdot 10^{-8}$
2-Nitroresorcinol	$1.59 \cdot 10^{-6}$
4-Nitroresorcinol	$1.04 \cdot 10^{-6}$

It will be observed that it makes relatively little difference to the *K* value whether a nitro group is placed *ortho* or *para* to a hydroxyl group. This indicates two significant features.

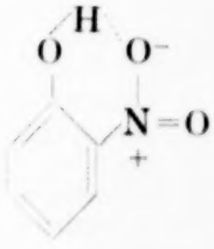
Firstly, it might have been expected that hydrogen bonding in the *ortho* compounds such as (VI) might preferentially stabilize the neutral forms of the *ortho* compounds.



(IV)



(V)



(VI)

Secondly, there is a possibility that the *ortho* nitro group will be forced out of the plane of the benzene ring and thus lose part of its potency as an acid-strengthening substituent. The results indicate that neither effect is large. This conclusion is fortified by the comparison of 2- and 4-nitro-resorcinol. In the former compound both hydroxyl groups are *ortho* to the nitro function and so distortion from planarity should be increased if it were of measurable significance.

By comparison, recent unpublished work[8] in the naphthalene series indicates that small "*ortho*" effects do occur with the nitro-naphthylamines and nitronaphthols. In each particular series, infrared studies and pK_a determinations show that intramolecular hydrogen bonding is present to a small degree with the 1-2 and 2-1 compounds, and to a more appreciable extent with 8-1 derivatives. These observations are confirmed by our stannous tin tests where the relative magnitude of the hydrogen bonding appears to be slightly greater with the 8-1 derivative than with either of the 1-2 or 2-1 compounds.

ACKNOWLEDGEMENTS

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SUMMARY

Thirteen nitronaphthols have been examined and found to be of use in the fluorimetric detection of stannous tin. The reagents were capable of detecting 10^{-4} to 10^{-5} g stannous tin whilst the nitro derivatives of 2-naphthol produced more intense fluorescence than the corresponding derivatives of 1-naphthol. Of the series examined, 8-nitro-1-naphthol was the least reactive, and this was attributed to the presence of intramolecular hydrogen bonding between the nitro and hydroxyl groups in this compound.

RÉSUMÉ

Les nitronaphtols ont été examinés en vue de leur utilisation comme réactif fluorimétrique de l'étain(II). On peut déceler ainsi jusqu'à 10^{-4} – 10^{-5} g de cet élément. Les dérivés nitrés du β-naphtol donnent une fluorescence plus intense que les dérivés de l'α-naphtol.

ZUSAMMENFASSUNG

Eine Anzahl Nitronaphtole wurden auf ihre Eignung als fluorimetrisches Nachweisreagenz für Zinn(II) geprüft. Es lassen sich hiermit noch 10^{-4} – 10^{-5} g Zinn nachweisen. Die Nitroderivate von β-Naphtol zeigen eine intensivere Fluoreszens als die entsprechenden Derivate des α-Naphtols.

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PROPERTIES OF RIBOFLAVIN PHOSPHATES

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Recently we have described[1,2] methods by which pure preparations of flavins can be obtained, and by which microgram quantities can be analysed. In the present investigation, the absorption spectra and the fluorescence of flavin phosphates were studied and their dissociation constants determined.

EXPERIMENTAL

Materials

Riboflavin-5′-phosphate (flavin mononucleotide, FMN) was prepared according to VISCONTINI *et al.*[3]. Riboflavin-5′-pyrophosphate (RPP) was a commercial preparation obtained from F.F. Firma, Florence. These substances were ultimately purified by several passages through a cation exchanger[1]. All manipulations were done in the dark.

Criteria of purity. The quantitative determination of FMN and RPP was routinely carried out by measuring the optical density at 260 and 450 mμ of the solutions under study. The qualitative determination was done by paper electrophoresis[2], and, in the experimental conditions used, the comparison of these two sets of data constituted an adequate criterion of purity.

Spectra, extinction coefficients and fluorescence

The absorption spectra (Fig. 1) were determined in a Beckman D.U. spectrophotometer, in 0.1*M* phosphate buffer pH 7.0. Readings were made every 2 mμ in the regions of the maxima and every 5 mμ elsewhere.

The extinction coefficients were determined on samples of the dry substances which had been kept in a desiccator *in vacuo* for several days, weighed and then dissolved to a suitable concentration. The values obtained are:

wavelength (mμ)	224	260	268	375	450	
ε (cm^2/mole · 10^3)	30.9	27.1	31.0	10.6	12.2	RPP
		27.1	30.6	10.4	12.2	FMN

The infrared spectra (Fig. 2) have been obtained in a Perkin Elmer IR spectrograph, Nujol medium. The effect of pH on the fluorescence of FMN and RPP was investigated in 0.1*M* phosphate–acetate–borate buffer[4] in the pH range from 2.0 to 12.0 Measurements were made in a Klett fluorimeter, lamp filter Corning glass 5543 and photocell filter Corning 3385. Results are shown in Fig. 3.

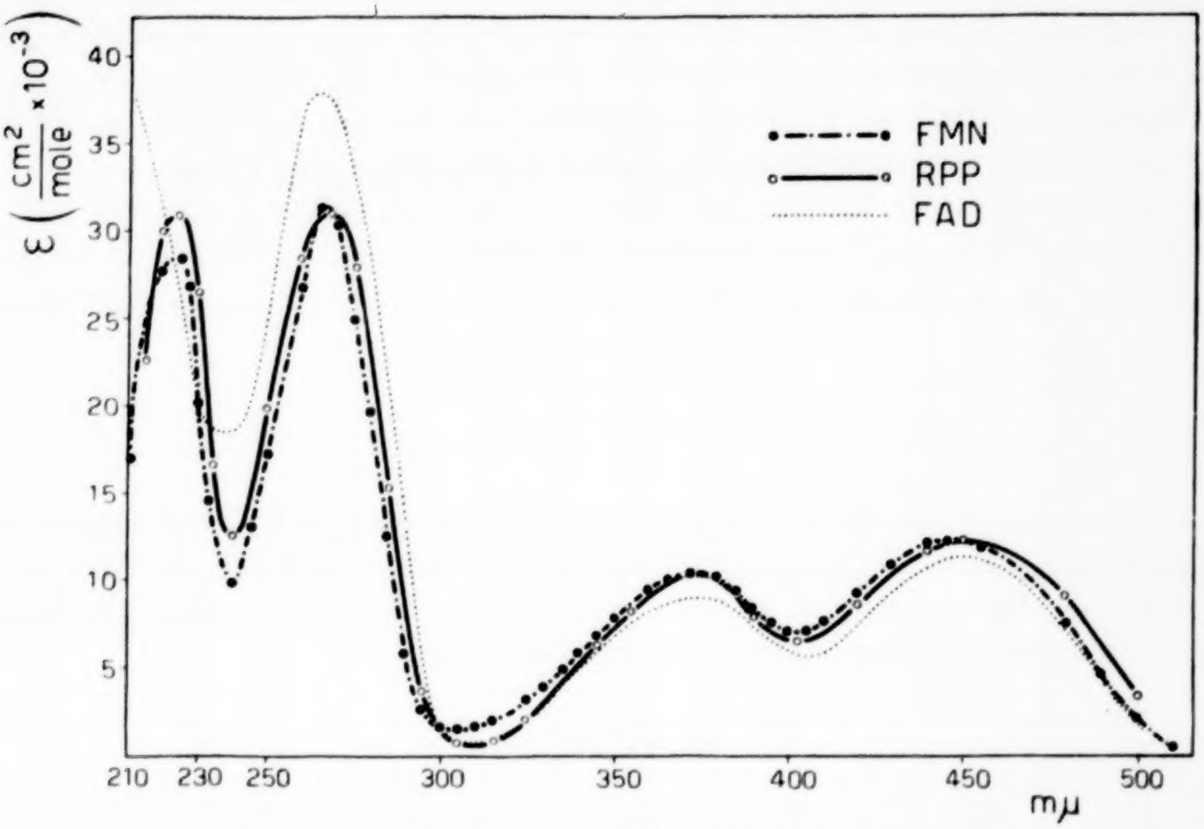

Fig. 1. Absorption spectra of RPP, FMN and FAD in 0.1 M phosphate buffer pH 7.0.

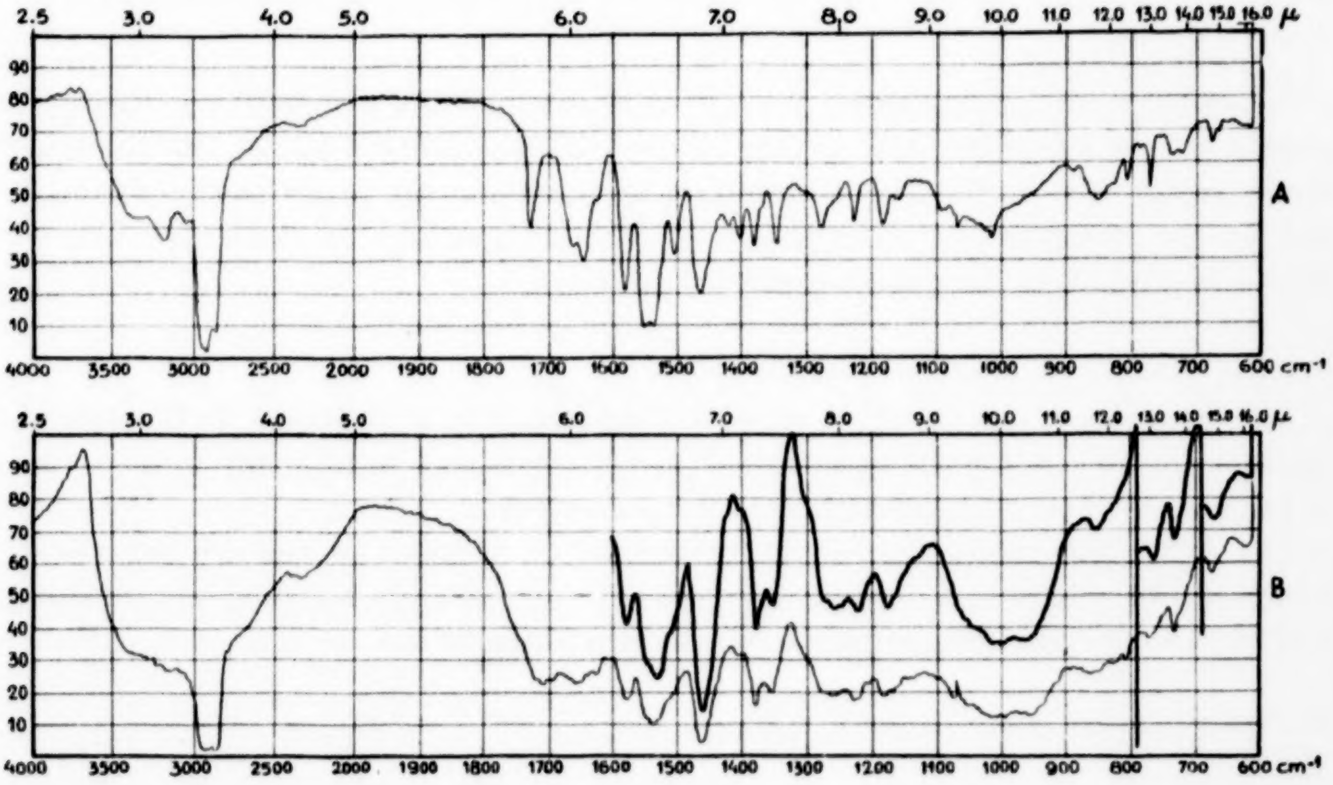

Fig. 2. Infrared spectra of FMN (A) and RPP (B).

Titration of FMN and RPP

Titrations were carried out with a Beckman or a Metrohm pH meter equipped with a glass electrode, at 18–20°. A microburette with a capacity of 1 ml was used. A magnetic stirrer kept the solution vigorously agitated. Back titration with HCl of the same normality as the NaOH used, was carried out in all experiments. Several samples were titrated for each substance. By keeping the volume small and using a fairly concentrated titrant, the corrections for the free hydrogen and hydroxyl ions in the pH range studied were kept quite small. Blank titration was carried out by collecting from the tubes which preceded and followed the peak of the sample in the last chromatographic passage, a volume of eluate identical to that of the sample and submitting it to the same treatment as the sample itself. The blank curve was substracted by volume from the sample curve, the difference curve representing the hydrogen ion-binding capacity of the samples as a function of the pH[5].

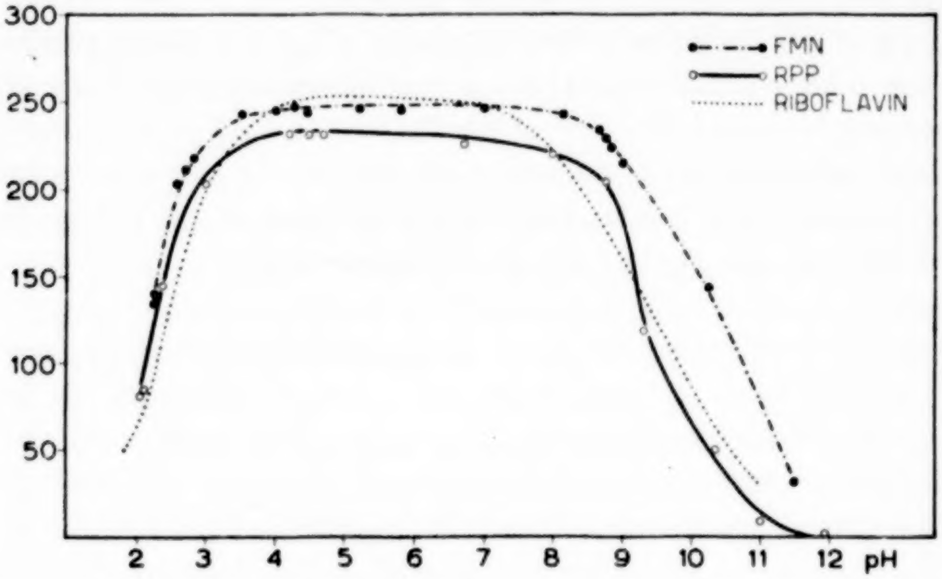

Fig. 3. Fluorescence of RPP, FMN and riboflavin at various pH. Ordinates give the per cent fluorescence as referred to a fluorescein standard.

FMN. The titration curve of FMN corrected for blank titration is shown in Fig. 4. It was obtained by titrating 9 ml of 0.0038*M* FMN with 0.3*N* NaOH and HCl. No hydrolysis occurred during titration. The curve shows two inflections with midpoints

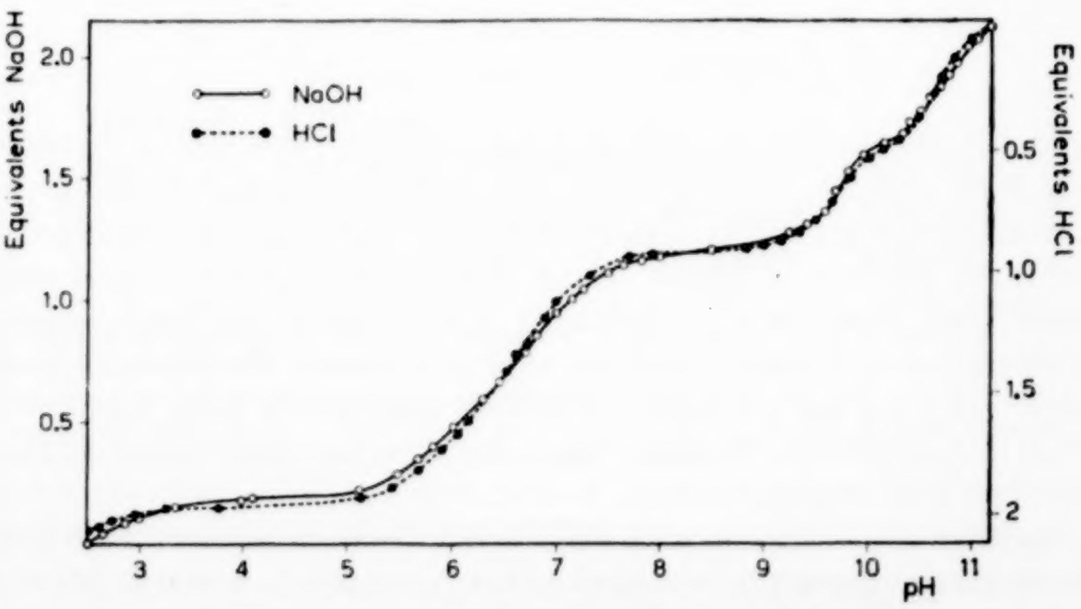

Fig. 4. Titration curve of FMN, corrected for a blank titration.

at pH 6.6 and 9.8. About 2.2 equivalents of titrant are needed to raise the pH from 2.52 to 11.16. A single clear equivalence point is seen, after addition of 1.15 equivalents. FMN has two ionizing groups in the isoalloxazine ring, with pK_a values of 9.8 and —0.2 in free riboflavin[6,7], and two acid functions in the phosphate moiety with pK_a values of 7.1 and 11.75 in free orthophosphoric acid. This last value is too high to be determined by direct titration[8].

At the initial pH of our solution a function with pK_a—0.2 is practically undissociated so that one may assume that the 2.3 equivalents of titrant are completely used for the other functions of FMN, one of which, having a p$K_a > 11$, is only partially titrated. The first inflection with midpoint at pH 6.7, is therefore ascribable to a function in the phosphoric radical while the inflection at pH 9.8 is due to one CO-NH group in the alloxan part of the isoalloxazine ring.

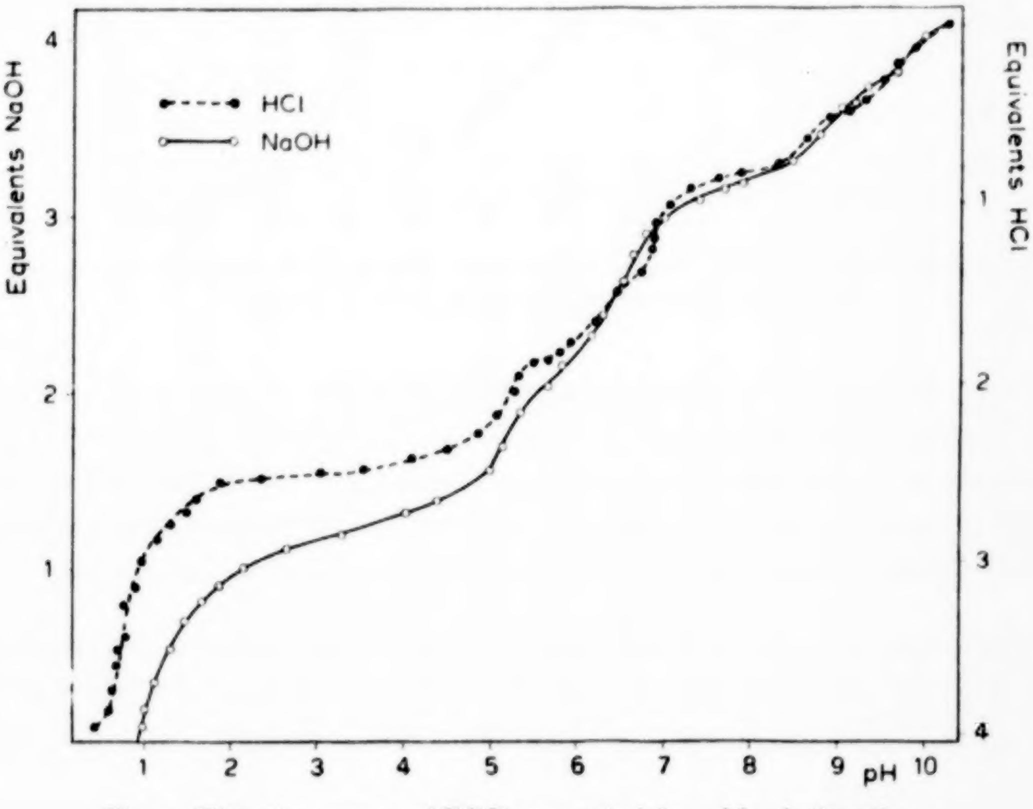

Fig. 5. Titration curve of RPP, corrected for a blank titration.

RPP. Fig. 5 shows the corrected titration curve of RPP, obtained by titrating 8 ml of 0.0065*M* RPP with 1*N* NaOH and HCl. No hydrolysis occurred during titration. The inflections, although not very sharp, are quite significant if considered in connection with the volumes of titrant. In the NaOH titration curve, four inflections are observed; only three reliable midpoints can, however, be fixed: about pH 6.2 (1.8 equiv.), pH 7.7 (2.8 equiv.) and pH 10.2 (3.5 equiv.). Equivalence points are distinct only after 1.2 and 3.2 equiv. A further equivalence point can however be discerned after 2.4 equiv. if the single hump due to overlapping groups in the region of pH 6.2 and pH 7.7 is resolved into two distinct curves according to PARKE AND DAVIS[6].

In the back titration diagram with HCl, four inflections are seen with midpoints at pH 9.85 (0.5 equiv.), pH 7.9 (1.2 equiv.), 6.2 (2.1 equiv.). A fourth possible midpoint can be placed at pH 1.8 (3.4 equiv.): it is known that an acid group with p$K_a < 2$

is titrated with difficulty using glass electrodes[9]. It is therefore possible that this last midpoint, which is not clearly seen in the NaOH titration curve, might have been missed during the titration with alkali.

Equivalence points are found after 0.85 and 2.6 equiv., and by resolving the straight line in the region from pH 6.5 to pH 8, also after 1.7 equiv. The inflections with midpoint at pH 1.8, 5.2, 7.8 – 7.9 can be ascribed to the acidic functions of the pyrophosphate radical, while the inflection with midpoint at pH 9.85 - 10.2 is probably due to the NH in the isoalloxazine ring, as in FMN.

CALCULATION OF THE DISSOCIATION CONSTANTS

Although theoretically all of the anionic species of a polybasic acid will be present at a given pH, the concentrations of one or more of the species will always be small enough at that pH to be neglected in a first approximation[8]. It is therefore possible to estimate the dissociation constants of a polybasic acid by a method of successive approximations utilizing the data obtained from an electrometric titration, the acid being dealt with at each pH as a monobasic acid[8]. The values thus obtained may then be used to estimate the concentrations of the components which were neglected in the first approximation. The appropriate corrections may then be made and the dissociation constants estimated a second time.

At the equivalence points only one species predominates, while, at intermediate points between them, two of the species predominate and it is in these regions that the most accurate estimations of the dissociation constants may be obtained. The method of calculation also permits the inclusion of one minor component in obtaining the first approximation of all the constants except the first one to be calculated.

The pH ranges chosen and the anionic species assumed to be present in first approximation calculations are given in Table I, the major components being printed in bold face type.

TABLE I

pH range	*Anionic species assumed present*					*Dissociation constant*
<5.5	$\mathbf{HRPO_4H_2}$	$\mathbf{HRPO_4H^-}$	$^-RPO_4H^-$			K_1
9–10	$HRPO_4H_2$	$\mathbf{HRPO_4H^-}$	$\mathbf{^-RPO_4H^-}$	$^-RPO_4^{-2}$		K_2
>10.5		$HRPO_4H^-$	$^-RPO_4H^-$	$^-RPO_4^{-2}$		K_3
<2	$\mathbf{HRP_2O_7H_3}$	$\mathbf{HRP_2O_7H_2^-}$				K_1
5–7	$HRP_2O_7H_3$	$\mathbf{HRP_2O_7H_2^-}$	$\mathbf{HRP_2O_7H^{-2}}$	$HRP_2O_7^{-3}$	$^-RP_2O_7^{-3}$	K_2
7.8 – 8.6			$\mathbf{HRP_2O_7H^{-2}}$	$\mathbf{HRP_2O_7^{-3}}$	$^-RP_2O_7^{-3}$	K_3
>9.6			$HRP_2O_7H^{-2}$	$\mathbf{HRP_2O_7^{-3}}$	$\mathbf{^-RP_2O_7^{-3}}$	K_4

$HRPO_4H_2$ and $HRP_2O_7H_3$ indicate the undissociated molecule of FMN and RPP respectively, $HRPO_4H^-$, $HRP_2O_7H_2^-$, $HRP_2O_7H^{-2}$, $HRP_2O_7^{-3}$ the anions deriving from the dissociation of the acid functions in the phosphate or pyrophosphate radical and $^-RPO_4H^-$, $^-RPO_4^{-2}$, $^-RP_2O_7^{-3}$ the anions originating from the dissociation of the acidic group in the isoalloxazine ring and of the acid functions in the phosphate or pyrophosphate radical.

The NaOH titration curve has been chosen for calculating the dissociation constants of FMN, since at the highest pH reached, one of the acid functions had not been fully titrated.

The initial solution of FMN is in the pH range where $HRPO_4H_2$ and $HRPO_4H^-$ are the only anionic species present in significant amounts.

Therefore, to a first approximation, at any given pH in that range,

$$A_0 + A_1 = RP \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where A_0 and A_1 are the amounts in micromoles of $HRPO_4H_2$ and $HRPO_4H^-$ present at the pH chosen, and RP the total amount of FMN used in the titration. OH_a equivalents of alkali are now added, which raise the pH of the solution but do not take it out of the range where $HRPO_4H_2$ and $HRPO_4H^-$ are the only major components. However the alkali does convert an equivalent amount of $HRPO_4H_2$ to $HRPO_4H^-$ (eqn. 4), the amounts of the two species becoming $(A_0 - OH_a)$ and $(A_1 + OH_a)$ respectively.

Therefore, if $[H^+]_i$ and $[H^+]_f$ are the initial and final hydrogen ion concentrations,

$$K_1 = [H^+]_i \, A_1 / A_0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

before adding acid and

$$K_1 = [H^+]_f \, (A_1 + OH_a) \; / \; (A_0 - OH_a) \quad . \; . \; . \; . \; . \; . \; . \quad (3)$$

after adding acid. Equating (2) and (3) and substituting $(RP - A_1)$ for A_0, a quadratic in A_1, is obtained. Although both solutions are positive, only one gives reasonable results in the calculation of K_1. Having now a value for K_1 it is possible to determine K_2 using much the same procedure as in estimating K_1. A quantity OH_b of alkali is added to the initial solution of FMN such that the resulting pH of the solution lies in the range 9–10, where $HRPO_4H^-$ and $^-RPO_4H^-$ are the major components, and $HRPO_4H_2$ the largest minor component. The alkali added is consumed in two reactions:

$$HRPO_4H_2 + OH^- \rightarrow HRPO_4H^- + H_2O \quad . \; . \; . \; . \; . \; . \; . \quad (4)$$

and

$$HRPO_4H^- + OH^- \rightarrow {}^-RPO_4H^- + H_2O \quad . \; . \; . \; . \; . \; . \; . \quad (5)$$

If an amount B of alkali is consumed in reaction (4), then $(OH_b - B)$ is consumed in reaction (5). If the hydrogen ion concentration at this point is designated by $[H^+]_{f2}$ then the following expressions are obtained for K_1 and K_2.

$$K_1 = [H^+]_{f2} \, (A_2 + OH_b + 2B) \; / \; (RP - A_1 - B) \quad . \; . \; . \; . \quad (6)$$

$$K_2 = [H^+]_{f2} \, (OH_b - B) \; / \; (A_1 - OH_b + 2B) \quad . \; . \; . \; . \; . \quad (7)$$

The third dissociation constant is extremely small and titration in the pH range which should be considered does not give reliable values, the substance being strongly hydrolyzed. The equations for calculating the dissociation constants of RPP are obtained in the same way using the HCl titration curve and making the appropriate assumptions with regard to the anionic species present (see Table I). On substituting the experimental data into approximate equations developed as described above, the following dissociation constants were obtained for FMN:

$$K_1 = 2.5 \cdot 10^{-7} \qquad pK_{a1} = 6.60$$
$$K_2 = 7.6 \cdot 10^{-11} \qquad pK_{a2} = 10.12$$

and for RPP, in a second approximation:

$$K_1 = 8.9 \cdot 10^{-3} \qquad pK_{a1} = 2.04$$
$$K_2 = 5.6 \cdot 10^{-7} \qquad pK_{a2} = 6.25$$
$$K_3 = 1.6 \cdot 10^{-8} \qquad pK_{a3} = 7.80$$
$$K_4 = 1.3 \cdot 10^{-10} \qquad pK_{a4} = 9.87$$

DISCUSSION

The extinction coefficients of RPP at the wavelengths of the maxima and at 260 mμ are in good agreement with those found for FMN and riboflavin by previous authors. The "flat" shape of the IR spectrum of RPP and the greater intensity of its bands at 1225 and 1260 cm^{-1}, as compared to FMN, reflect the presence of a pyrophosphate. The specific absorption of the P-O-P group, which is placed by some authors at about 970–940 cm^{-1}, is however masked by the absorption of the phenyl group, and the free OH groups of the phosphoric and pyrophosphoric radicals do not allow the study of bands in the 1000 cm^{-1} region where the P-O-C alkyl bond should absorb. The pH–fluorescence curves of FMN and RPP are quite similar to those found for riboflavin by previous authors[7,10-12].

According to KUHN AND MORUZZI[12] the fluorescent form of riboflavin is the dipolar ion. The dissociation constants of the CO-NH group in the alloxan ring of FMN and RPP, as determined from the slopes in the alkaline range of the fluorescence curves, correspond to the values obtained by titrimetric methods.

The pK_a for the imino group is much higher in FMN than in RPP and riboflavin, where the values are nearly the same. This is probably due to the influence of a weakly acid function, with pK_a >11, which is found in FMN but not in RPP or riboflavin. The value of the dissociation constants of RPP and FMN found in the present investigation, are in good agreement with those given for free ortho- and pyrophosphoric acid and for riboflavin by previous authors[6,7,12,13]. The data presented are apparent ionization constants (K_a'): they can however be directly compared to true dissociation constants (K_a) since in the present case the ionic strength of the solution at the end of the titration was sufficiently low[5,14] to keep the deviation from K_a within the experimental error.

It should be noted that K_1 in FMN and K_3 in RPP have higher values than the corresponding constants of the free inorganic acid. This effect may reasonably be ascribed to the lack of one of the acid functions existing in the free acid, which in RPP and FMN forms an ester linkage with ribitol.

ACKNOWLEDGEMENTS

This investigation was aided by grants from the Rockefeller Foundation, to which grateful acknowledgement is made.

SUMMARY

The u.v., visible, and i.r. spectra, the extinction coefficients, fluorescence, and dissociation constants of pure riboflavin-5′-phosphate and riboflavin-5′-pyrophosphate are studied and discussed.

RÉSUMÉ

On a étudié les spectres d'absorption u.v., visible et infrarouge, les coefficients d'extinction molaire, la fluorescence et les constantes de dissociation de phosphates de riboflavine.

ZUSAMMENFASSUNG

Es wurden die u.v.-, sichtbaren- und i.r.-Absorptionsspektren sowie die Fluoreszenz von reinem Riboflavin-5′-phosphat und Riboflavin-5′-pyrophosphat untersucht und deren Extinktionskoeffizienten und Dissoziationskonstanten bestimmt. Die Ergebnisse werden diskutiert.

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POLAROGRAPHY OF 4-BENZOTHIAZOLOL

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A study of the analytical chemistry of 4-benzothiazolol was undertaken in order to determine the usefulness of this reagent and to compare its analytical behaviour with structurally similar compounds such as 8-quinolinol. As a part of this study, the reduction of 4-benzothiazolol at the dropping mercury electrode was investigated mainly to establish the conditions under which it could be used as a reagent for the amperometric titration of metal ions.

EXPERIMENTAL

Preparation of compound

4-Benzothiazolol was prepared by the method described by Erlenmeyer and Überwasser[1], and recrystallized several times from ethanol: m.p. 143°. The infrared absorption spectrum of the compound was determined for purposes of characterization. A Perkin-Elmer Model 21 recording spectrophotometer with sodium chloride optics was used to record the spectrum of the compound in KBr pellets. Fig. 1 and Table I give results obtained.

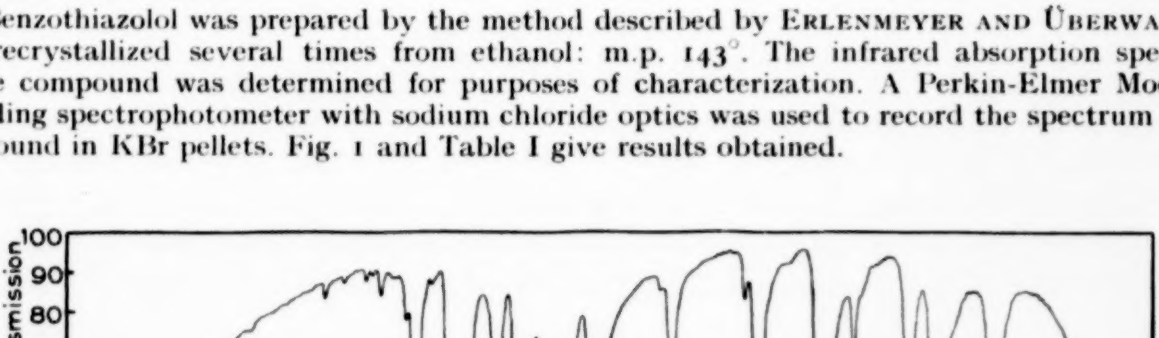


Fig. 1. Infrared spectrum of 4-benzothiazolol.

Apparatus

All polarograms were recorded on a Leeds and Northrup Model E Electrochemograph. A voltage span of 2 V was used in all experiments with the damping switch at zero. Nitrogen was used to remove dissolved oxygen from the solutions. One arm of an H-type cell was used as the electrolysis vessel and was separated from the reference saturated calomel electrode by means of a fritted glass disc and an agar plug saturated with KCl. No corrections were made for the *iR* drop since the resistance of the cell was small. All polarograms were recorded at 25° ± 0.05°, except those used for determining temperature coefficients. The capillary used had a drop time of 2.64 seconds and a mass rate of flow of 2.94 mg/sec in a Na_2HPO_4–citric acid buffer at pH 6.90, at an applied potential of 1.55 V under a corrected mercury head of 44.24 cm. pH values were determined with a Beckman Model G pH meter standardized with a potassium acid–phthalate buffer of pH 4.01.

Buffer solutions

McIlvaine buffers in the pH range 2–8 were made up from 0.2*M* Na_2HPO_4 and 0.1*M* citric acid. The composition of the buffer solutions used is given in Table II. Less than 1% ethanol was

TABLE I

INFRARED ABSORPTION SPECTRUM OF 4-BENZOTHIAZOLOL

Intensity:	*Strong* cm^{-1}	*Medium* cm^{-1}	*Weak* cm^{-1}	*Very weak* cm^{-1}
	3125	1480	3050	1905
	1600	1420	1150	1820
	1570	1355	955	1735
	1450	1320	848	1715
	1245	1285		1685
	942	1200		1520
	878	1170		866
		1050		
		802		
		782		
		743		
		736		
		670		

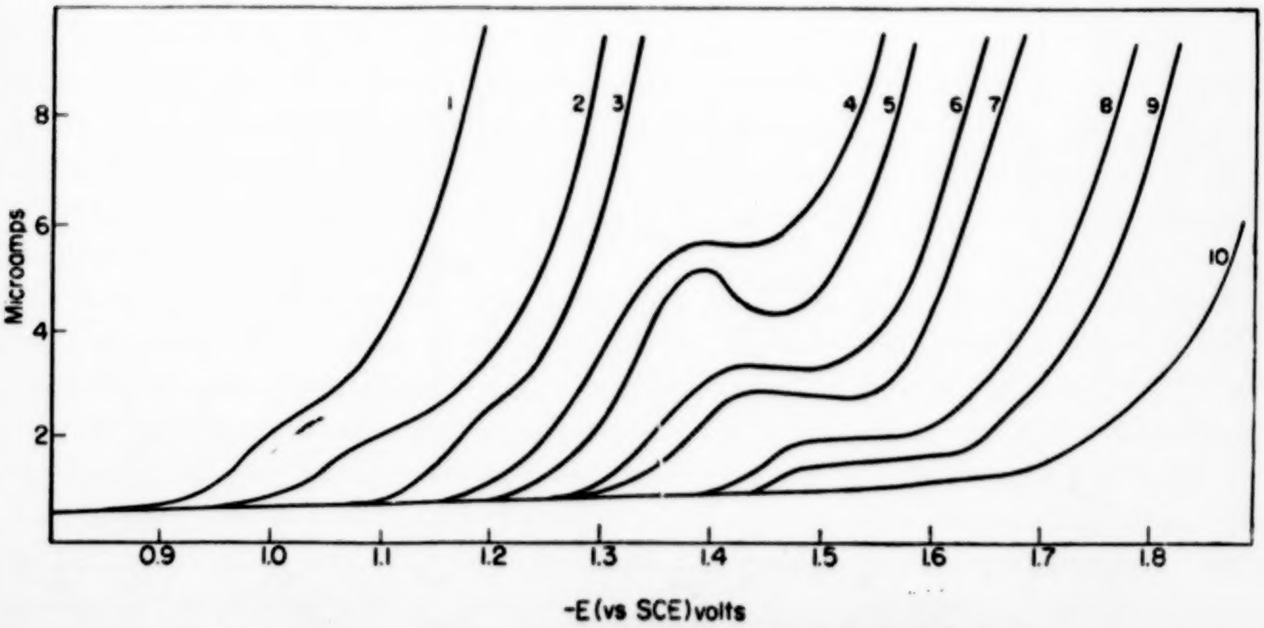


Fig. 2. Polarograms of 1·10⁻⁴*M* 4-benzothiazolol. (1) pH 2.25; (2) pH 3.30; (3) pH 4.25; (4) pH 4.88; (5) pH 5.30; (6) pH 5.61; (7) pH 6.00; (8) pH 6.82; (9) pH 7.30; (10) pH 8.10.

TABLE II

VARIATION OF THE HALF-WAVE POTENTIAL WITH pH

pH	*Buffer components*		$-E_{1/2}$ *V vs. S.C.E.*
	Na_2HPO_4 *M*	*Citric acid* *M*	
2.25	0.004	0.088	1.06
2.70	0.020	0.080	1.09
3.09	0.040	0.070	1.11
3.30	0.050	0.065	1.14
3.55	0.060	0.060	1.15
4.00	0.070	0.055	1.24
4.25	0.077	0.052	1.27
4.40	0.080	0.050	1.31
4.60	0.084	0.048	1.34
4.88	0.090	0.045	1.38
5.30	0.100	0.040	1.43
5.45	0.102	0.039	1.45
5.61	0.106	0.037	1.45
6.00	0.111	0.035	1.48
6.20	0.120	0.030	1.49
6.70	0.130	0.025	1.54
6.80	0.140	0.022	1.55
6.90	0.143	0.020	1.55
7.09	0.147	0.017	1.57
7.30	0.160	0.010	1.58

added to all solutions in order to ensure that the 4-benzothiazolol was in solution. The buffer components were examined for polarographically reducible impurities before use. The concentration of 4-benzothiazolol was $1 \cdot 10^{-4} M$, except in those cases in which the dependence of the diffusion current on concentration was determined.

RESULTS AND DISCUSSION

Fig. 2 shows that solutions of 4-benzothiazolol were reducible at pH values greater than 5.3. In general, the behaviour of this compound is less complicated than that

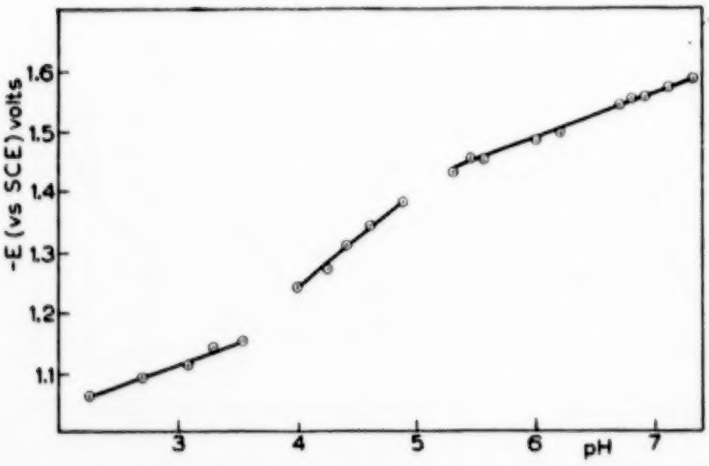


Fig. 3. Effect of pH on the half-wave potential of $1 \cdot 10^{-4} M$ solutions of 4-benzothiazolol.

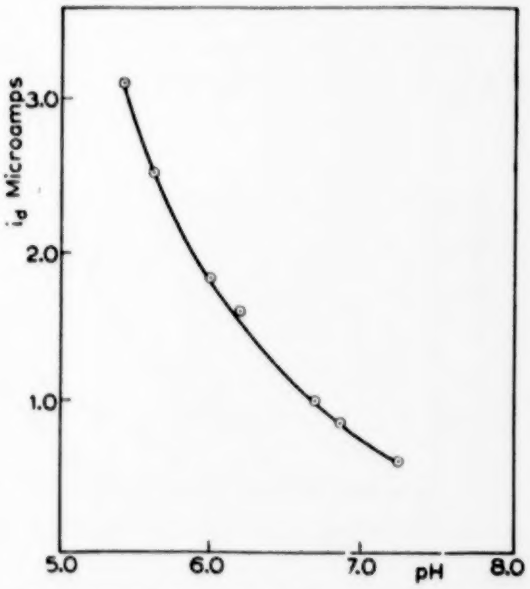
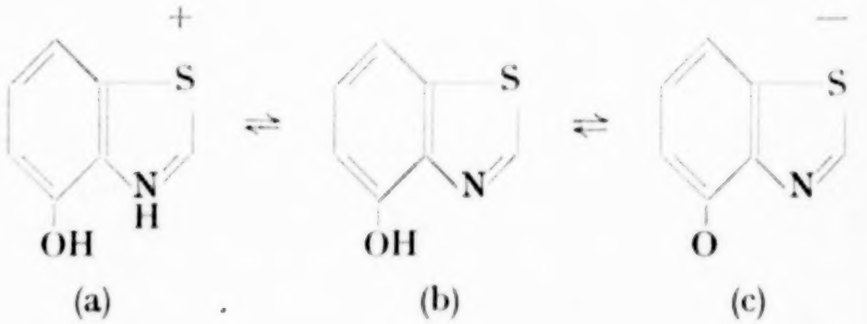


Fig. 4. Effect of pH on the diffusion current of $1 \cdot 10^{-4} M$ solutions of 4-benzothiazolol.

of 8-quinolinol[2]. In acid solutions, between pH 2 and 5, a small wave appears and its height increases with increase in pH. This is probably a catalytic wave similar to that observed in acid solutions in the reduction of several 8-quinolinols[3]. Analysis of this wave was made difficult by hydrogen discharge in acid solutions and also by the appearance of a pronounced maximum at a pH of about 4.5. This maximum can be suppressed with small amounts of Triton X-100, but the wave height and half-wave potential are altered. The half-wave potential of this wave in acid solutions shifts to more negative potentials with increasing pH. Fig. 3 and Table II show the effect of pH on the half-wave potential, over the complete pH range examined. At a pH of about 6 a well-defined wave is obtained; the height of this wave decreases, and the half-wave potential becomes more negative, with increase in pH.

4-Benzothiazolol consists of a mixture of the protonated ion, the neutral molecule, and the anion in solution as shown in eqn. (1). The dissociation constants K_{NH} and K_{OH} have been found by a spectrophotometric method to be 1.20 ± 0.05 and 8.85 ± 0.05 respectively[4]. From these values it can be shown that at a pH of 2.2, 91% of the 4-benzothiazolol exists in the neutral form, and at a pH of 9.85 only 9% of the 4-benzothiazolol remains as the neutral species. Fig. 2 shows that at a pH of 8.1 no appreciable reduction wave was observed at an instrument sensitivity of 20 μA per 100 chart divisions. Fig. 4 shows the manner in which the wave height decreases with increase in pH. It is therefore reasonable to infer that at pH values greater than 5.3, it is the neutral species (b) of 4-benzothiazolol that undergoes reduction at the dropping mercury electrode. Although it would be reasonable to expect that the protonated ion (a) would be more easily reduced, hydrogen discharge precluded direct observation of this. Of course, the negative charge in the anionic species (c) would increase the difficulty of reduction of this form.

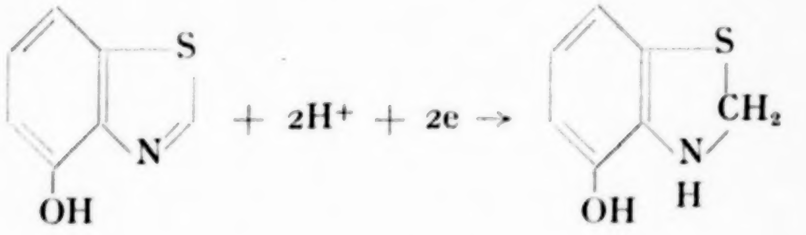


. . . (1)

The well-defined reduction wave obtained at a pH of 6.9 was free of maxima, and its characteristics were studied in greater detail. The diffusion current at pH 6.9 was determined at various heights of the mercury column. The wave height was corrected for residual current variation with the mercury head, and the height of the mercury column was corrected for back pressure. The determination of $i_d/(h_{corr.})^{0.5}$ at six different values of $h_{corr.}$ between 30 and 53 cm of mercury, gave an average value of 0.0528 ± 0.001. This indicates that the reduction wave obtained at this pH is governed by diffusion.

The diffusion currents at pH 6.9 were also determined over a temperature range from 10° to 47°; the temperature coefficient calculated from the compound interest formula is +1.6% per degree. This confirms the fact that the wave is diffusion controlled.

The number of electrons involved in this reduction can be calculated by means of the Ilkovic equation. Assuming that the diffusion coefficient of the compound is the same as that of quinaldinic acid[2], *i.e.*, $0.80 \cdot 10^{-5}$ cm^2/sec, the number of electrons involved in the reduction is 2. The reduction process that is most probable is shown in eqn. (2).



. . . . (2)

A plot of the applied potential against log $\{i/(i_d - i)\}$ for the reduction wave at pH 6.9 did not give a straight line, thereby indicating that the above reduction process is probably irreversible.

Attempts were made to identify the reduction product formed at the dropping mercury electrode. A $1 \cdot 10^{-4} M$ solution of 4-benzothiazolol was reduced at the dropping mercury cathode for 8 hours at an applied potential of −1.6 V and at a pH of 6.9 with a nitrogen atmosphere maintained over the solution. The ultraviolet absorption spectrum was determined before and after the polarographic reduction; the absorption spectrum of the compound and its reduced form were identical from 220 mμ to 240 mμ and 260 mμ to 320 mμ. Between 240 mμ and 250 mμ small differences were observed; a new peak appeared in the reduced solution and the peak at 257 mμ underwent a small hypsochromic shift. A controlled cathode potential reduction was carried out on a large scale at a mercury pool cathode separated from the anode compartment by means of a salt bridge. The potential of the mercury cathode was maintained manually at −1.6 V, measured against an external saturated calomel

TABLE III

PROPORTIONALITY BETWEEN DIFFUSION CURRENT AND CONCENTRATION OF 4-BENZOTHIAZOLOL AT pH 6.80

Concentration (C) mmoles/l	*Diffusion current (i_d) μA*	*i_d/C*
0.10	0.87	8.70
0.20	1.74	8.70
0.24	2.08	8.67
0.30	2.60	8.67
0.32	2.77	8.66
0.36	3.12	8.67
0.40	3.45	8.63
0.48	4.15	8.65
0.56	4.82	8.61

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electrode. A nitrogen atmosphere was maintained above the solution during the electrolysis. The ultraviolet absorption spectrum of the 4-benzothiazolol solution before and after reduction was essentially the same as that observed in the polarographic reduction. Even after prolonged reduction, no further changes in the spectrum were observed. However, these differences between 240 mμ and 260 mμ were not sufficiently marked to warrant interpretation.

The height of the well-defined reduction wave at pH 6.9 was proportional to the concentration of 4-benzothiazolol from 0.1 to 0.6 mmoles/l, and the diffusion current constant for this wave was 2.86 (Table III). This wave could therefore be used for the amperometric titration of metal ions such as Fe^{+3}, Co^{+2}, Ni^{+2}, Zn^{+2}, Cu^{+2}, Hg^{+2}, and Ag^{+}, which were found to form precipitates with 4-benzothiazolol in an acetate–acetic acid buffer at pH 4.6. The usable reduction wave for 8-quinolinol is obtained at pH values greater than 9, and in this respect, 4-benzohiazolol seems to be more suitable than 8-quinolinol for the amperometric titration of metal ions.

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SUMMARY

The polarographic behaviour of 4-benzothiazolol at the dropping mercury electrode has been compared with that of 8-quinolinol. A well-defined, irreversible cathodic wave, suitable for the determination of 4-benzothiazolol, was obtained at pH 6.8. The characteristics of this wave indicated that it was due to a two-electron reduction of 4-benzothiazolol to 2,3-dihydro-4-benzothiazolol.

RÉSUMÉ

Le comportement polarographique de l'hydroxy-4-benzothiazol, à l'électrode à gouttes de mercure, a été comparé à celui de l'hydroxy-8-quinoléine. On obtient au pH 6.8 une vague cathodique bien définie, irréversible, pouvant servir au dosage de ce composé.

ZUSAMMENFASSUNG

Das polarographische Verhalten von 4-Hydroxybenzothiazol an der Quecksilbertropfelektrode wurde mit dem von 8-Oxychinolin verglichen. Bei pH 6.8 wurde eine gut definierte, irreversible kathodische Welle erhalten, welche zu dessen Bestimmung verwendet werden kann.

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RAPID DETERMINATION OF CHLORIDE IN SILICA OR OTHER SOLIDS

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INTRODUCTION

A rapid procedure was required for the determination of inorganic chloride in silica and other solids. Chloride can be determined rapidly after it is separated from interfering elements, but the separation step is usually lengthy and requires considerable attention. It was decided, therefore, to develop a method which would enable rapid separation of the chloride by evolution from the rest of the sample.

Proposed method

It is known that if a solid is treated with a sulfuric–nitric acid mixture and heated to fumes, any inorganic and most organic chlorides will be evolved. The evolved chloride can be collected in a scrubber and determined by titration or colorimetrically. It was hoped that the procedure would be rapid and precise. It was also anticipated that this procedure could be extended to the analysis of other halides and work is in progress to develop such procedures.

RESULTS

Evolution procedure

A method was developed using the principles outlined above. A diagram of the apparatus is shown in Fig. 1. The procedure was found to be rapid (total time, 20 min) and to give good precision as illustrated in Table I.

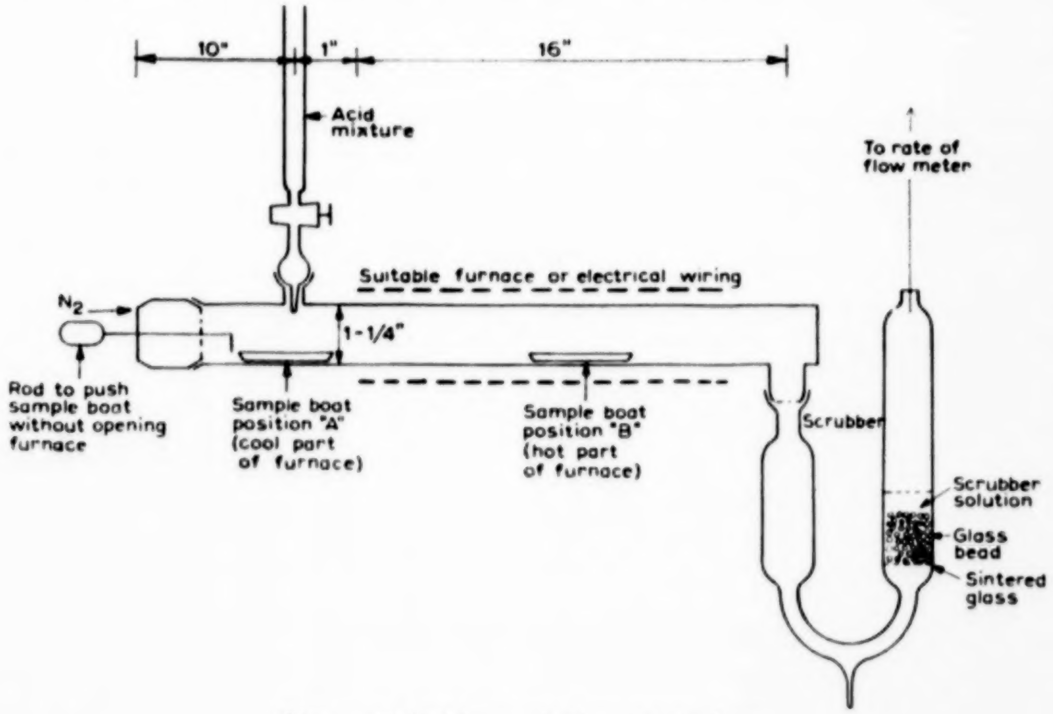
10"
1"
16"
Acid mixture
To rate of flow meter
Suitable furnace or electrical wiring
N_2
1-1/4"
Rod to push sample boat without opening furnace
Sample boat position "A" (cool part of furnace)
Sample boat position "B" (hot part of furnace)
Scrubber
Scrubber solution
Glass bead
Sintered glass

Fig. 1. Chloride evolution procedure.

TABLE I

RESULTS OBTAINED ON REPETITIVE ANALYSIS OF A SAMPLE CONTAINING APPROXIMATELY 0.6% Cl

(1) 0.618	(5) 0.590	(8) 0.602	(11) 0.598
(2) 0.626	(6) 0.598	(9) 0.620	(12) 0.600
(3) 0.615	(7) 0.605	(10) 0.618	(13) 0.610
(4) 0.598			

2 = 0.022%, 95% confidence.
Average = 0.61 wt. %.

A significant advantage of the method is that samples up to 1.5 g can be taken. This is particularly useful when the homogeneity of the sample is in doubt.

Scrubber

Dilute sodium carbonate solutions or deionised water were both successfully used as scrubbing agents. The chloride content of the scrubber was determined satisfactorily either by a potentiometric silver nitrate titration, or by a colorimetric procedure. These enabled the procedure to be used for wide ranges of chloride content, *i.e.*, from the part per million level to the high wt.% level. The majority of interfering elements are eliminated by this procedure because they form non-volatile sulfates.

RECOMMENDED PROCEDURE

A typical procedure is as follows:

Reagents

Sulfuric acid + nitric acid. 90 ml sulfuric acid (conc.) + 10 ml nitric acid (conc.). *Sodium carbonate solution.* 2% AnalaR sodium carbonate in deionized water. *Deionized water.* Water deionized with a resin column. *Silver nitrate solution.* 0.0282*N* $AgNO_3$. 1 ml = 1 mg Cl made from Aculates. *Nitrogen.* Cylinder nitrogen. *Acetone.* AnalaR acetone.

For the analysis of a silica sample containing 0.5% chloride, weigh out approximately 1 g of sample into a porcelain boat. Insert the boat into the furnace tube beneath the acid dropper. Add the acid dropwise to the sample, traversing the full length of the boat until the sample is just wetted.

Allow the sample to soak for 1 min in the cool zone of the furnace. Push the sample into the hot part of the furnace, and beat for 15 min. Temperature of the hot zone of the furnace is 590°F.

Nitrogen is passed down the tube throughout the entire operation at a rate of 1 l/min.

Evolved chloride is collected in 100 ml of scrubbing solution.

At the end of the run, the contents of the scrubber are transferred to a beaker, the scrubber is washed several times with a few ml of fresh scrubber solution. The combined scrubber and wash solutions are adjusted to pH 2 with HNO_3. An equal volume of acetone is added to the beaker and the chloride is titrated potentiometrically with standard silver nitrate solution. For samples with low chloride content, *i.e.* 1 mg, a small amount of chloride (about 1 mg) may be added to the scrubber prior to titration and subsequently substracted during the calculation. This gives a sharper potentiometric break and makes the end-point easier to determine.

Blank

A blank determination can be run by going through the entire procedure but leaving out the sample. This enables the chloride content of the nitrogen and other reagents to be determined and subtracted from the apparent chloride content of the sample.

Colorimetric procedure

For very low chlorides, a suitable sample weight is treated as described above. The chloride content of the scrubber is determined colorimetrically using mercuric thiocyanate and ferric ammonium sulfate[1].

CALCULATIONS

$$\% \text{ Cl}^- = \frac{\text{wt. chloride (g)} \times 100}{\text{wt. sample (g)}}$$

Titration procedure:

$$\text{Wt. chloride} = \frac{\text{No. ml AgNO}_3 \text{ taken} \quad (1 \text{ ml AgNO}_3 = 1 \text{ mg Cl}^-)}{1000}$$

Colorimetric procedure:

$$\text{Wt. chloride} = \text{Concn. of Cl}^- \text{ solution (from calibration chart)} \times \text{volume scrubber solution}$$

ACKNOWLEDGEMENTS

The author wishes to express thanks to A. F. DE CASTRO, JULIA ELLERBE, L. J. JONES, J. R. WAGNER for suggestions used in completing this project.

SUMMARY

A rapid evolution method has been developed for the determination of chloride. This procedure can be applied to a wide range of chloride concentrations.

RÉSUMÊ

Une méthode rapide est proposée pour le dosage des chlorures à des concentrations variées.

ZUSAMMENFASSUNG

Es wird eine Schnellmethode zur Bestimmung von Chloriden bei verschiedenen Konzentrationen beschrieben.

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HIGH FREQUENCY TITRATIONS

II. THE MERCURY(II)-THIOCYANATE REACTION

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In a previous communication[1], it has been shown that the high frequency (oscillometric) technique can be suitably employed for the end-point detection in a precipitation reaction between Ag^+ and SCN^-. The chief advantage of this procedure is the ability to determine milligram-quantities of silver or thiocyanate in dilute solutions.

Because mercury(II) thiocyanate is slightly dissociated, it was thought interesting to study this reaction oscillometrically. Volumetrically, the titrations are performed either way using ferric iron as the indicator. During the titration, $Hg(SCN)^+$ is usually present and at the end-point precipitation of $Hg(SCN)_2$ is likely to occur. The end-point is less sharp than in the corresponding silver–thiocyanate reaction owing to the complexation of excess thiocyanate ion as $Hg(SCN)_3^-$ and $Hg(SCN)_4^{-2}$. As such titrations have a comparatively low accuracy in dilute solutions[2], KOLTHOFF[3] has shown that at low temperatures the results are scarcely influenced by the nitric acid concentration of the solution although it is preferable to keep it low. Notwithstanding, the mercury(II)–thiocyanate reaction is widely used for ordinary precision work in organic and inorganic analysis provided not too dilute solutions are used.

In general, instrumental methods for end-point detection are superior in being independent of visual observation of color changes, and the high frequency technique possesses an additional advantage due to the absence of contact between the electrodes and the solution without sacrificing the sensitivity in measuring characteristic changes in the composition of the system. The present paper describes the high frequency end-point in the titration of Hg(II) with thiocyanate and *vice versa*, for the microdetermination of either of these ions in dilute solutions.

EXPERIMENTAL

Apparatus

A Sargent model V Oscillometer, operating at 110–120 V and 60 cycles, was used in the present work. The titrations were carried out in a Type B (100-ml) cell.

Reagents

All the chemicals used were of reagent grade. In the mercury(II) nitrate solution the nitric acid concentration was kept minimum. The mercury(II) solution was titrated with 0.1 *N* KSCN or NH_4SCN using ferric alum indicator. Low concentration solutions were obtained by successive dilution.

Procedure

The instrument was allowed to stabilize for 30–60 min before use. The clean dry cell was placed in the cell holder and the needle pointer adjusted to center zero scale position. A desired volume of mercuric nitrate solution was transferred into the cell and the total volume brought to 100 ml with water. After the initial instrument (capacitance) reading was recorded, small increments of ammonium or potassium thiocyanate solution were added from the buret. The system was stirred carefully after each addition of the reagent. Readings were taken before and after the equivalence point and the experimental end-point obtained from a plot of volume of the reagent added *versus* the instrument reading. Reverse titrations were carried out in an exactly similar manner.

Representative curves are shown in Figs. 1–4 and the experimental results for the estimation of mercury and thiocyanate are entered in Tables I and II.

TABLE I

HIGH FREQUENCY TITRIMETRIC DETERMINATION OF MERCURY(II) BY THIOCYANATE

Final molarity of Hg(NO$_3$)$_2$ solution, M	*Mercury (mg)*		
	actual	*found*	*difference*
1/1,596	12.5975	12.7300	0.1325
1/3,186	6.2951	6.2550	0.0401
1/6,372	3.1475	3.1275	0.0200
1/10,621	1.8885	1.8755	0.0130
1/15,933	1.2585	1.2340	0.0245
1/31,866	0.6295	0.6055	0.0240

TABLE II

HIGH FREQUENCY TITRIMETRIC DETERMINATION OF THIOCYANATE BY MERCURY(II)

Final molarity of KSCN solution, M	*KSCN (mg)*		
	actual	*found*	*difference*
1/1,523	6.3651	6.4860	0.1209
1/3,047	3.1820	3.1910	0.0090
1/15,239	0.6365	0.6335	0.0030
1/30,385	0.3192	0.3070	0.0122

DISCUSSION

Fig. 1 shows that during the course of a straight titration of mercury(II) nitrate *versus* thiocyanate, the instrument (capacitance) reading first decreases and then rises continuously. The single inflection denotes the quantitative formation of mercuric thiocyanate. These titrations could be performed in the presence of nitric acid provided its overall normality did not exceed about 1/300*N*. In the reverse titration also, the instrument reading exhibits a slight initial decrease and then a continuous increase. The magnitude of increase is small in the beginning and larger thereafter (*cf.* Fig. 2). Here, the reaction appears to take place in two stages, the first break corresponding approximately to the stoichiometry of Hg^{+2}:SCN^- as 1:1 and hence to the formation of $Hg(SCN)^+$. The second break indicates the normal mercuric thiocyanate, $Hg(SCN)_2$. The occurrence of the first break is perhaps due to the tendency of $Hg(SCN)^+$ complex to be comparatively more stable in the presence of excess thiocyanate, which is not the case in the straight titration. A few experiments were carried out using mercury(II) acetate solution. Fig. 3 shows that during the titration

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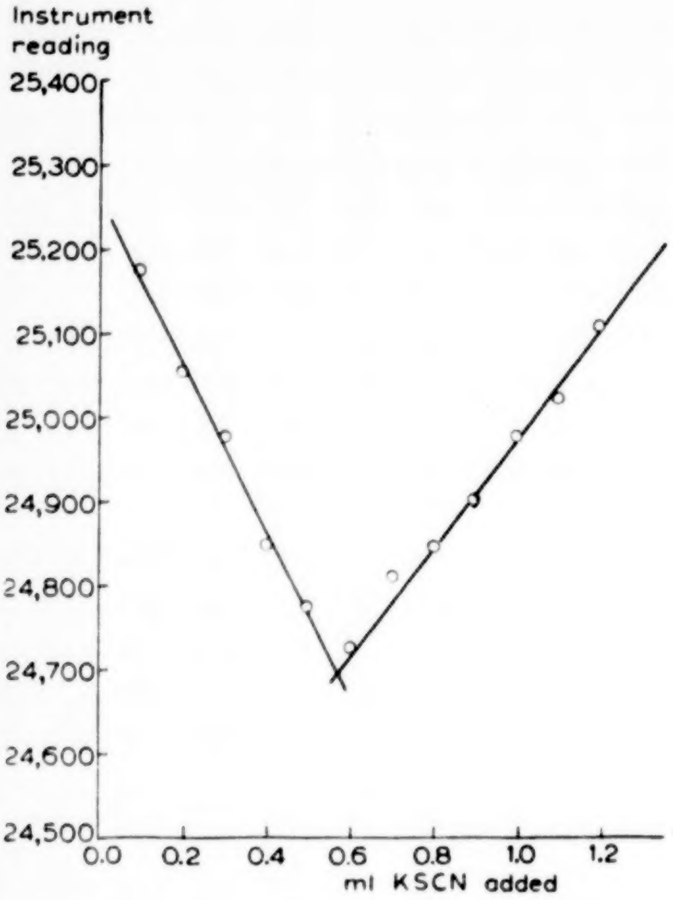

Fig. 1. High frequency titration of 100 ml of 1/10,621M Hg(NO$_3$)$_2$ with 0.03281M KSCN. End-point: theoretical 0.574 ml, from graph 0.570 ml.

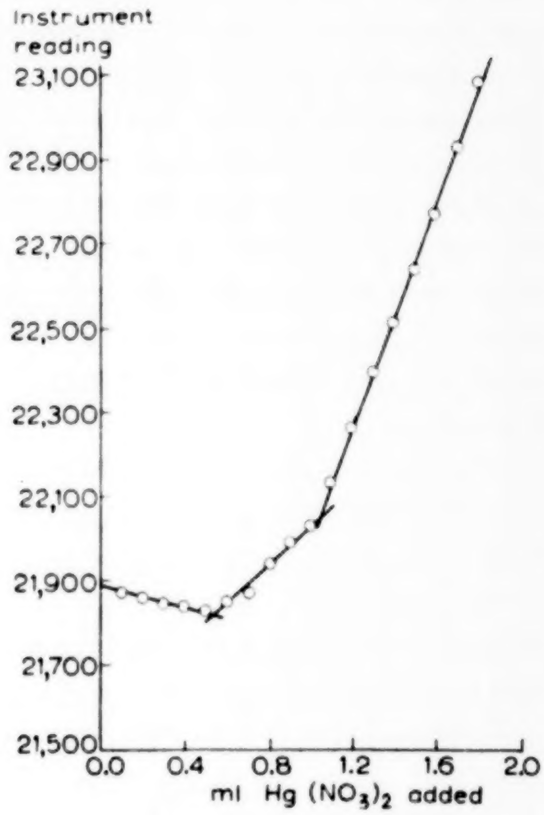

Fig. 2. High frequency titration of 100 ml of 1/15,239M KSCN with 0.003125M Hg(NO$_3$)$_2$. End-point: theoretical 1.050 ml, from graph 1.045 ml.

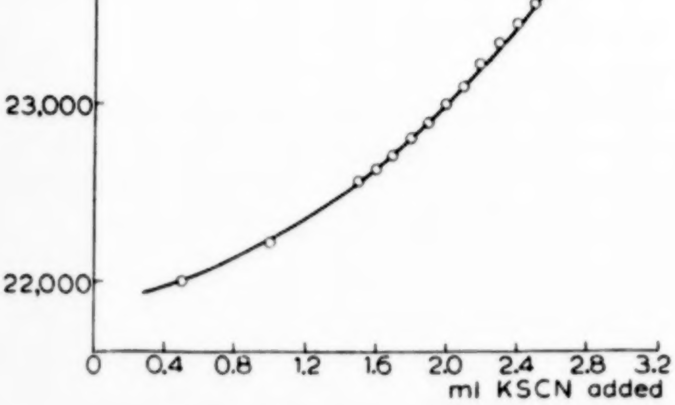

Fig. 3. High frequency titration of 100 ml of 1/2,000M Hg(CH$_3$COO)$_2$ with 0.050M KSCN. End-point: theoretical 2 ml.

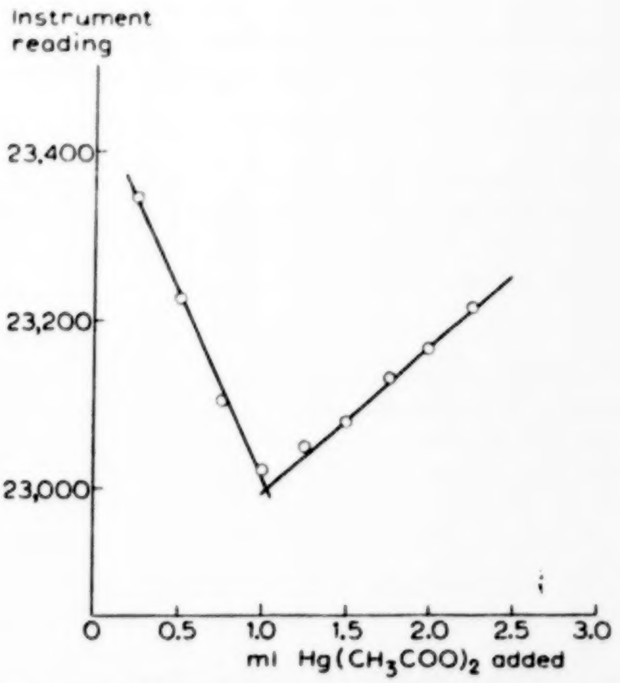

Fig. 4. High frequency titration of 100 ml of 1/1,995M KSCN with 0.0514M Hg(CH$_3$COO)$_2$. End-point: theoretical 1.025 ml, from graph 1.025 ml.

of mercury(II) acetate against thiocyanate, the instrument characteristics change uniformly with no means of determining the end-point. However, mercury(II) acetate can be used as a titrant for the determination of thiocyanate, the inflection point corresponding to the formation of neutral mercuric thiocyanate (*cf.* Fig. 4). In all the experiments, there was no visible precipitate at or near the end-point. Under the present conditions of ionic concentrations and dilution, it is difficult to say conclusively whether or not the complexes $Hg(SCN)^+$, $Hg(SCN)_3^-$ and $Hg(SCN)_4^{-2}$ are formed. Only in one case is the existence of $Hg(SCN)^+$ suspected (*vide supra*), whereas in no case is there an indication of the formation of negatively charged complexes. Hence either these complexes are only transiently formed, or the high frequency method, like other electrometric methods, is unsuitable to record their step-wise formation.

Data in Tables I and II show that very small quantities of mercury or thiocyanate may be determined with a reasonable accuracy. Only in the dilution ranges 1/16,000 and 1/32,000*M*, does the error become about 2 and 4% respectively. The mercury(II)–thiocyanate reaction, employing the high frequency end-point, can therefore be adopted for a rapid titrimetric analysis in high dilutions — a circumstance in which the indicator method generally fails.

Further work on the halide and the cyanide complexes of mercury(II) is in progress.

ACKNOWLEDGEMENT

We are indebted to Boyd Professor Dr. PHILIP W. WEST for research facilities and interest in the work.

SUMMARY

Soluble complex-formation of mercury(II) thiocyanate has been studied oscillometrically. The titration of mercury(II) nitrate with thiocyanate gives one inflection corresponding to the formation of $Hg(SCN)_2$, while in the reverse titration the formation of $Hg(SCN)^+$ is also indicated. The method is useful for a rapid determination of very small quantities of mercury or thiocyanate in highly dilute solutions. The titrations can be effected in presence of nitric acid provided its total acidity in the system does not exceed about 1/300*N*. Further work on the mercury(II)–halide and mercury(II)–cyanide reactions is in progress.

RÉSUMÉ

La formation du complexe soluble mercure(II)–thiocyanate a été étudiée par oscillométrie. La méthode peut être utilisée pour le dosage rapide de très petites quantités de mercure ou de thiocyanate. Le titrage peut s'effectuer en présence d'acide nitrique, si l'acidité totale du système ne dépasse pas 1/300*N* environ.

ZUSAMMENFASSUNG

Die Bildung des löslichen Quecksilber(II)–Thiocyanat Komplexes wurde oscillometrisch untersucht. Diese Methode kann zur Schnellbestimmung sehr kleiner Mengen Quecksilber oder Thiocyanat angewandt werden. Die Titration kann in Gegenwart von Salpetersäure ausgeführt werden, wobei aber die Gesamt-Acidität des Systems 1/300*N* nicht überschreiten darf.

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SUR LA STABILITÉ THERMIQUE DES ÉTALONS ANALYTIQUES
VII*

CLÉMENT DUVAL

avec la collaboration technique de

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Dans cette septième série, nous présentons une étude relative aux 12 corps suivants: iodate de baryum, saccharose, tartrate de sodium, oxalate neutre de potassium, acétate de cuivre, chlorure de cadmium, sulfate d'ammonium, nitrate ferrique, persulfate d'ammonium, carbonate de thallium, acétate d'uranyle, carbonate de potassium.

Toutes ces substances ont été chauffées sur l'une des thermobalances à enregistrement photographique, avec montée linéaire à raison de 300° par heure et avec des poids de substance de l'ordre de 200 mg. Les spectres infrarouges ont été réalisés sur poudre, avec de la vaseline comme agglomérant, entre 6 et 15 μ, sur le spectromètre Perkin-Elmer 12C avec optique de chlorure de sodium.

Iodate de baryum

Ce corps, cristallisé avec une molécule d'eau, a été préconisé comme étalon pour le dosage par la méthode de Karl Fischer. La courbe représentative de la thermolyse (Fig. 1) avait déjà été tracée[1] mais les vitesses d'échauffement n'étant pas les mêmes, nous observons aux hautes températures une divergence que nous voulons préciser. La déshydratation commence à 43°; elle est à peine sensible à 60°, s'accentue vers 79°, puis on observe un changement de courbure lorsque les trois quarts de l'eau de cristallisation ont disparu. La perte du reste de l'eau s'effectue beaucoup plus paresseusement et n'est vraiment terminée qu'à 320°. De 320° à 476° se présente le palier horizontal relatif à l'iodate anhydre, puis la réaction de Rammelsberg se manifeste:

$$5\ Ba(IO_3)_2 \rightarrow Ba_5(IO_6)_2 + 9\ O_2 + 4\ I_2$$

avec violence, notamment à 610°, pour s'achever à 666°; alors commence le palier du paraperiodate de baryum qui est stable au moins jusqu'à 960°, limite de notre expérience.

Le spectre infrarouge présente les bandes suivantes: 728 (F), 784 (épaulement), 801 (f), 811 (aF) cm^{-1}.

Saccharose

Nous avons chauffé ce corps à plusieurs reprises en nous servant de produits commerciaux divers (sucre de canne, sucre de betterave, en morceaux, cristallisé, en poudre, sucre d'érable, etc.). Les courbes tracées sont toutes identiques et ressemblent beaucoup à celle de l'amidon, du coton hydrophile, du papier, etc.

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* Pour le sixième mémoire de cette série, voir *Anal. Chim. Acta*, 20 (1959) 20.

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En ce qui concerne le saccharose (Fig. 2), on observe un poids constant jusqu'à 231°, le produit ayant déjà bruni à cette température, puis le dégagement gazeux, la combustion commencent, se montrent en pleine activité à 327° et les réactions s'achèvent vers 619°, le creuset étant sensiblement vide. A 900°, il ne reste qu'une minime particule d'une substance minérale (chaux?) et de charbon non brûlé.

Le spectre infrarouge présente un assez grand nombre de bandes: 849 (F), 865 (F), 907 (TF), 919 (épaulement), 939 (F), 988 (TF), 1001 (aF), 1039 (f), 1050 (f), 1069 (f), 1104 (f), 1121 (f), 1158 (f), 1204 (f), 1233 (aF), 1273 (aF), 1318 (aF), 1347 (aF) cm^{-1}.

Tartrate neutre de sodium

Le tartrate de sodium actif renferme au départ deux molécules d'eau qu'il conserve jusqu'à 57°. Il fond alors dans son eau de cristallisation, puis cette eau est évacuée progressivement jusqu'à 154° avec changement de direction quand une molécule d'eau a disparu. Le sel anhydre est stable jusqu'à 255°; alors commence une perte brutale d'oxyde de carbone, d'eau de constitution; vers 309° on a un mélange de charbon et de carbonate de sodium. Ce charbon brûle progressivement jusqu'à 700° environ. Le carbonate de sodium résiduel commence à son tour à se dissocier vers 875° (au lieu de 840° lorsque ce corps est chauffé seul à la même vitesse) (Fig. 3).

Dans son spectre infrarouge nous relevons les bandes suivantes: 770 (large), 804 (aF), 849 (aF), 885 (F), 919 (TF), 990 (TF), 1064 (F), 1110 (F), 1203 (aF), 1239 (aF), 1273 (aF), 1337 (f), 1408 (f), 1603 (TF) cm^{-1}.

Oxalate neutre de potassium

Ce sel contient exactement une molécule d'eau de cristallisation qu'il n'abandonne qu'au-dessus de 100° et jusqu'à 168°. Alors s'étend le palier horizontal de l'oxalate anhydre $K_2C_2O_4$, jusqu'à 500°. La dissociation se produit alors libérant une molécule d'oxyde de carbone suivant:

$$K_2C_2O_4 \rightarrow CO + K_2CO_3$$

Ce carbonate de potassium fournit un palier horizontal jusqu'à 914° au moins (Fig. 4).

Dans la région du sel gemme nous relevons les bandes suivantes: 772 (TF), 1308 (F), 1587 (TF) cm^{-1}.

Acétate de cuivre

Ce sel cristallise avec une molécule d'eau qu'il commence à perdre à 107°. La déshydratation se produit ensuite progressivement jusqu'à 167°. Là, le sel anhydre n'est pas stable; il commence tout de suite à perdre de l'oxyde de carbone, puis une explosion se manifeste vers 270° et donne naissance à un mélange de cuivre et d'oxyde cuivreux qui se réoxyde progressivement à partir de 296°. On arrive à l'oxyde cuivrique CuO, noir, dont le poids se maintient constant au-dessus de 510° (Fig. 5).

Son spectre infrarouge présente trois bandes: 1031 (aF), 1050 (aF), 1600 (TF) cm^{-1}.

Chlorure de cadmium

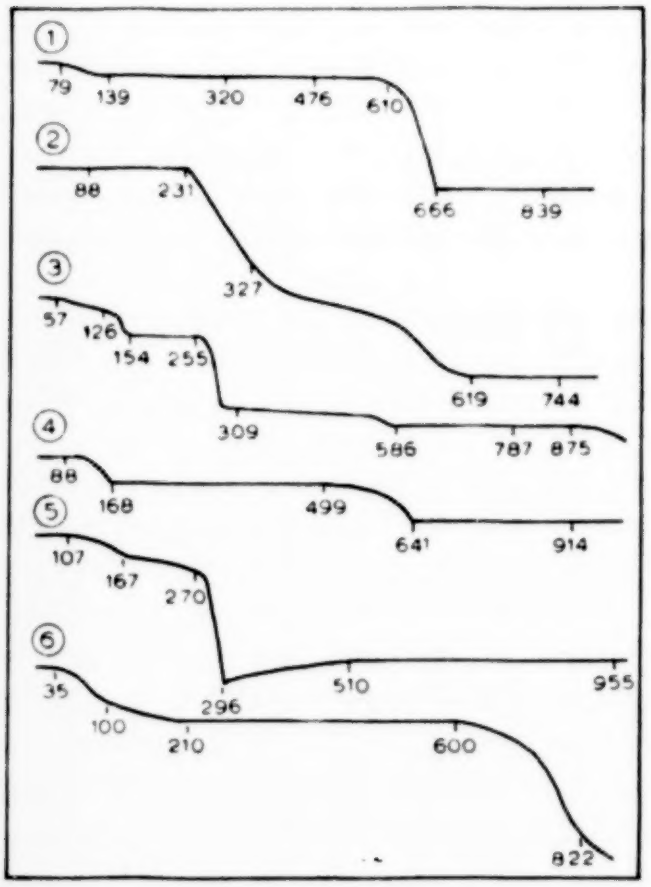
Le chlorure de cadmium $CdCl_2 \cdot 2.5H_2O$, n'est pas stable sous cet état d'hydratation; dès 35° il perd progressivement cette eau jusqu'à 210°. Vient alors le palier du chlorure anhydre qui s'étend jusqu'à 600°. Alors commence la dissociation avec oxydation, donnant naissance à l'oxyde CdO qui se sublime à son tour et vers 1012° le creuset est vide (Fig. 6).

Le chlorure de cadmium est transparent dans la région spectrale étudiée.

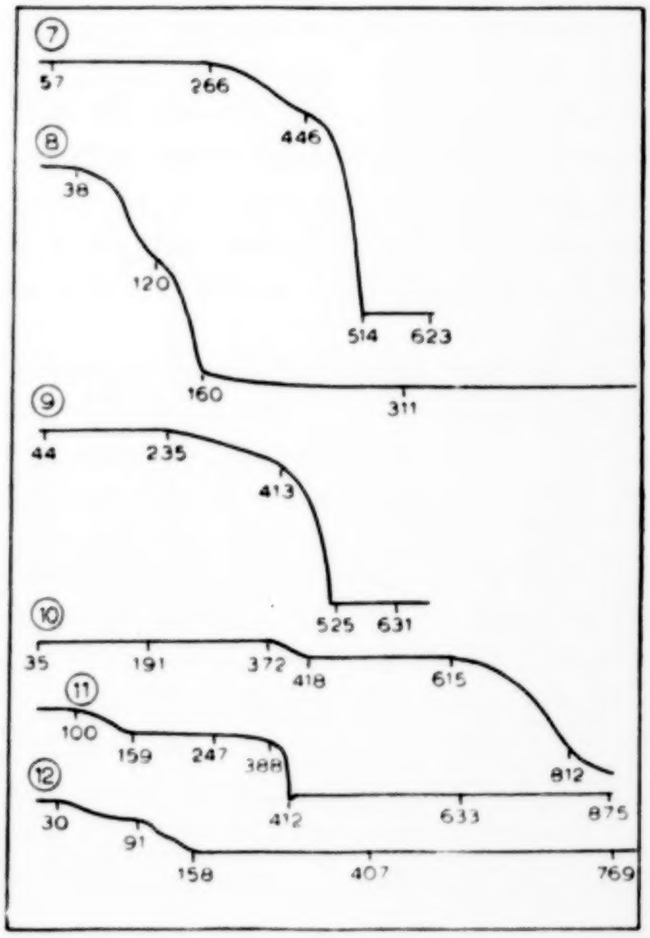
Sulfate d'ammonium

Lorsque ce sel est tout seul, il commence à se sublimer et à se détruire à 266°. Il n'en est pas de même, comme nous le savons (voir le VIème mémoire de cette série), lorsque ce sulfate provient de la dissociation du sel de Mohr ou de l'alun ferrique. La dissociation se fait en deux temps: de 266° à 446° environ, départ d'ammoniac, puis de 446° à 514°, départ explosif d'anhydride sulfurique ou de ses produits de dissociation. Le creuset est complètement vidé à 514° (Fig. 7).

Le spectre infrarouge, dans la région étudiée, présente les bandes suivantes: 1050 (F), 1099 (épaulement), 1387 (F) (confondue avec une bande de la vaseline).



Figs. 1-6.



Figs. 7-12.

Nitrate ferrique

Il est à peu près impossible de faire directement une liqueur titrée avec ce sel car il perd son eau de cristallisation dès 38°. A 120° il commence à se dissocier en perdant les vapeurs rutilantes et la réaction est même explosive vers 144°. Elle se ralentit ensuite vers 160° et les dernières traces d'oxydes de l'azote étant enlevées progressivement, on arrive à l'oxyde de fer vers 311°, poids constant qui se maintient ensuite jusqu'à 1000°. Quoique d'apparence hygroscopique, le sel initial renferme, suivant les calculs effectués sur le graphique, environ 9 molécules d'eau (poids moléculaire calculé 392 pour un poids théorique de 398, correspondant à $Fe(NO_3)_3 \cdot 9H_2O$, l'oxyde final étant Fe_3O_4) (Fig. 8).

Le spectre infrarouge présente trois bandes: 837 (TF), 1040 (épaulement), 1327 (F et large) cm^{-1}.

Persulfate d'ammonium

Ce sel est anhydre et stable jusqu'à 235°. Il se transforme alors en sulfate d'ammonium et le reste de la courbe est identique à celui de la Fig. 7. Le creuset est vidé à 514°, après départ explosif de SO_3 (Fig. 9).

Dans son spectre infrarouge nous relevons les bandes suivantes: 859 (F), 1050 (F) (sulfate), 1183 (TF), 1407 (aF) cm^{-1}.

Carbonate de thallium

Ce sel est anhydre et stable jusqu'à 372° (température plus élevée que celles données par différents auteurs.) Après cela, le thallium s'oxyde et il y a simultanément perte de gaz carbonique et brunissement du résidu. Il apparait le composé $CO_3Tl_2 \cdot Tl_2O_3$ qui a déjà été signalé parmi les carbonates basiques de thallium. Ce dernier composé offre un palier horizontal allant de 418° à 615°. Alors commence une nouvelle décomposition assez compliquée: le carbonate de thallium restant se dissocie, l'oxyde de thallium trivalent Tl_2O_3 se réduit et l'oxyde de thallium monovalent résultant Tl_2O se sublime. Le creuset n'est pas encore complètement vidé à 1000° (Fig. 10).

Le spectre infrarouge accuse les bandes suivantes: 844 (aF), 1033 (aF), 1059 (f), 1327 (f) cm^{-1}.

Acétate d'uranyle

L'acétate d'uranyle répond bien à la formule $UO_2(CH_3CO_2)_2 \cdot 2H_2O$; il est stable jusqu'à 100°. L'eau de cristallisation s'échappe jusqu'à 159°. Alors commence le palier du sel anhydre qui s'étend jusqu'à 247°. La dissociation de l'acétate se produit alors très lentement jusqu'à 388°, puis d'une manière explosive ensuite et à 412° il ne reste plus que l'oxyde U_3O_8 mélangé sans doute d'un peu d'oxyde UO_2, car la courbe de thermolyse (Fig. 11) accuse un petit crochet et une légère réoxydation.

Le spectre infrarouge, entre 6 et 15 μ présente les bandes suivantes: 937 (épaulement), 944 (F), 971 (f), 1028 (aF), 1059 (aF), 1375 (F), 1475 (F) cm^{-1}.

Carbonate de potassium hydraté

Les cristaux d'hydrate sont habituellement comptés à 1.5 H_2O. L'échantillon que nous avons eu en mains était probablement un mélange de ce dernier et d'hexahydrate. Les calculs effectués sur la courbe (Fig. 12) s'accordent avec la formule $K_2CO_3 \cdot 3H_2O$. Cette eau disparait progressivement et sans former de palier jusqu'à 158°. Alors commence le palier du carbonate anhydre qui s'étend jusque vers 875°.

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Son spectre infrarouge révèle les bandes suivantes: 846 (F), 881 (aF), 1022 (F), 1059 (F), 1151 (F), 1604 (TF) cm^{-1}.

RÉSUMÉ

Nous avons donné la courbe de thermolyse et le spectre infrarouge entre 6 et 15 μ, pour 12 substances proposées jusqu'ici comme étalons en chimie analytique.

SUMMARY

The thermolysis curves and infra-red spectra between 6 and 15 μ are given for 12 substances that are used as standards in analytical chemistry.

ZUSAMMENFASSUNG

Der Verlauf der Thermolyse und die IR-Spektren zwischen 6 und 15 μ werden für 12 Ursubstanzen der analytischen Chemie beschrieben.

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Reçu le 25 juin 1958

THE THERMOLYSIS OF AMMONIUM 12-MOLYBDOPHOSPHATE

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There is some question as to the composition and drying temperature for ammonium 12-molybdophosphate. DUVAL[1] found that the precipitated compound corresponded to the formula, $(NH_4)_3(MoO_3)_{12}PO_4 \cdot 2HNO_3 \cdot H_2O$. On studying the pyrolysis of this compound, he found that nitric acid and water were evolved up to 180° and that from 180° to 410° the compound, $(NH_4)_3(MoO_3)_{12}PO_4$, was obtained. Above 410°, ammonia and water were lost with subsequent formation of the $24MoO_3 \cdot P_2O_5$ level at 812°. However, an oxide ignition temperature of 600–850° was deemed permissible.

The thermal decomposition of $(NH_4)_3PO_4 \cdot 12MoO_3$ *in vacuo* was investigated by GREGG AND STOCK[2]. They found that after heating the sample to constant weight at 180°, the rate of weight loss increased gradually up to 380° and then became very rapid above 470°. At 630°, the oxide level, $24MoO_3 \cdot P_2O_5$, was obtained. In many respects, this work was similar to that of DUVAL except for the thermal decomposition of the compound below 180°.

The recent work of STOCKDALE[3] revealed that the composition of ammonium 12-molybdophosphate depended upon the precipitate washing conditions. If the precipitate was washed with dilute nitric acid and dried at 140°, it corresponded to the formula, $(NH_4)_2H[P(Mo_3O_{10})_4] \cdot H_2O$; if washed with a dilute solution of ammonium nitrate and dried at 280°, the composition corresponded to the formula, $(NH_4)_3[P(Mo_3O_{10})_4]$. There was little difference in the gravimetric factors for the two com-

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positions, hence, either of the two compounds could be used in gravimetric analysis.

Since the studies of STOCKDALE[3] differ from previous work on ammonium 12-molybdophosphate, it was of interest to reinvestigate this compound on the thermobalance.

EXPERIMENTAL

Reagents

All chemicals used were of analytical reagent grade quality.

Preparation of ammonium 12-molybdophosphate

The same procedure as described by STOCKDALE[3] was followed. Samples of the dilute HNO_3 and dilute NH_4NO_3 washed precipitates were either air dried at room temperature for 24 h or dried in an oven at 160° for 2 h.

Thermobalance

An automatic recording thermobalance as previously described was used[4]. Sample sizes ranged from 70 to 90 mg and were run in duplicate or triplicate. A linear heating rate of 5.0° per minute was employed. During the pyrolyses, a slow stream of air was passed through the furnace.

DISCUSSION

The thermograms of the compounds are given in Fig. 1.

Ammonium 12-molybdophosphate, HNO_3 washed

The air-dried compound (Fig. 1/A) began to evolve loosely held water at 60°. After a fairly rapid weight loss, a horizontal weight level was observed from 160° to

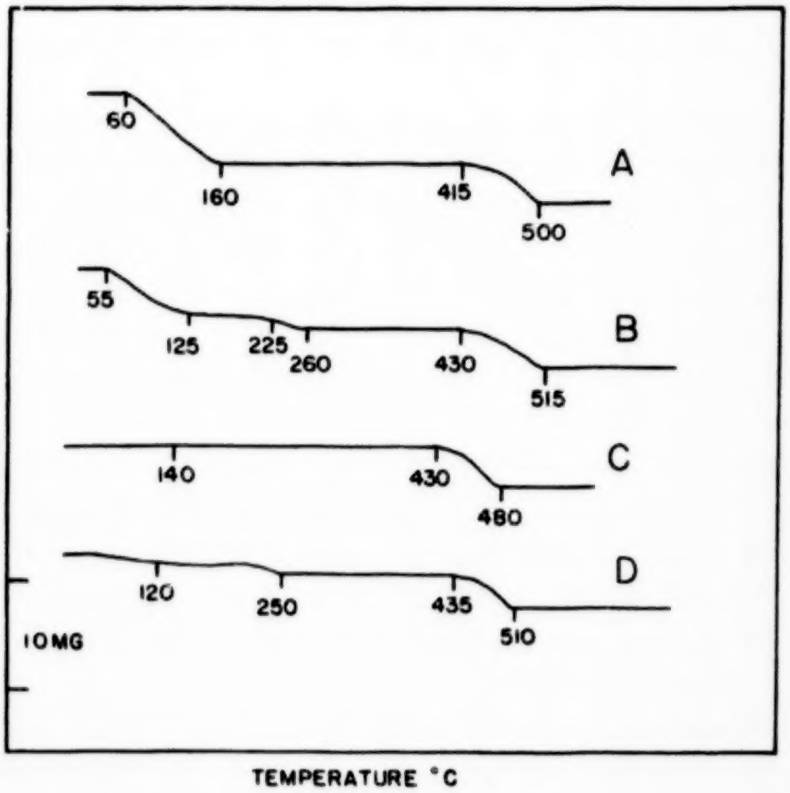

Fig. 1. Thermograms of ammonium 12-molybdophosphate.
A. HNO_3 washed, air dried.
B. NH_4NO_3 washed, air dried.
C. HNO_3 washed, oven dried.
D. NH_4NO_3 washed, oven dried.

415° which corresponded to the formula, $(NH_4)_2H[P(Mo_3O_{10})_4]\cdot H_2O$. Beyond 415°, additional weight loss occurred to give the oxide level, $P_2O_5\cdot 24MoO_3$, beginning at 500°. The drying temperature of 140° cited by STOCKDALE[3] appears to be a little too low to effectively dry the compound.

The oven-dried (at 160°) compound (Fig. 1/C) gave a thermogram similar to that of the air-dried compound, but did not show the loss of the loosely held water. Decomposition of the compound to the oxide began at 430° and was complete at 480°.

Ammonium 12-molybdophosphate, NH_4NO_3 washed

The air-dried compound (Fig. 1/B) began to evolve loosely held water at 55°. The rate of weight loss was rapid at first, but became much slower between 125° and 225°. However, a horizontal weight level was not obtained so that this region of the curve could not be used for drying temperature. Apparently, the compound is slowly losing NH_4NO_3 left by the wash liquid. Above 225°, the NH_4NO_3 is evolved more rapidly, resulting in a horizontal weight level from 260° to 430°, which corresponded to the formula, $(NH_4)_3[P(Mo_3O_{10})_4]$. Total decomposition of the compound began at 430°, resulting in the $P_2O_5\cdot 24MoO_3$ level at 515°. The drying temperature of 280° recommended by STOCKDALE[3] appears to be suitable, but slightly higher temperatures may be employed.

The oven-dried (at 160°) compound (Fig. 1/D) exhibited a pyrolysis curve which was similar to that of the air-dried compound except for the initial loss of water. Ammonium nitrate was slowly evolved up to 250°, the temperature at which the anhydrous triammonium 12-molybdophosphate level began. Total disruption of the compound began at 435°, resulting in the $P_2O_5\cdot 24MoO_3$ level at 510°.

General

The results of this study differ from the pyrolysis curve as previously reported by DUVAL[1]. However, this may be due to the different methods used to precipitate the ammonium 12-molybdophosphate. A similar situation was found in the case of oxine molybdophosphate[5]. The precipitation process is no doubt very complex and still requires further study. However, if the method of STOCKDALE[3] is employed, then the pyrolysis curves reported in this study should apply. Any deviation from this procedure may seriously affect the composition of the precipitate and also the drying temperature.

SUMMARY

The thermal decomposition of ammonium 12-molybdophosphate, prepared under various conditions was studied on the thermobalance. For the HNO_3 washed precipitate, a drying temperature of 160° to 415° was recommended; for the NH_4NO_3 washed compound, a drying temperature of 260° to 430° should be employed.

RÉSUMÉ

L'auteur a examiné, à l'aide d'une thermobalance, la décomposition thermique du phosphomolybdate d'ammonium, préparé dans diverses conditions.

ZUSAMMENFASSUNG

Die thermische Zersetzung von Ammonium-phosphormolybdat, unter verschiedenen Bedingungen hergestellt, wurde mit Hilfe einer Thermowaage untersucht.

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REMARQUES SUR LA COMMUNICATION PRÉCÉDENTE DE M. WENDLANDT

CLÉMENT DUVAL

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1. Lorsque j'ai entrepris en 1946 l'étude de thermogravimétrie publiée dans *Analytica Chimica Acta* je me suis servi des modes opératoires publiés jusqu'en 1945. Je ne peux donc pas avoir étudié le précipité préparé par STOCKDALE en 1958.

2. Même en utilisant un mode opératoire semblable, les courbes de thermobalance ne sont comparables que si l'on s'en tient aux mêmes vitesses de chauffage, au même poids, à la même épaisseur de précipité et à la même nature de creuset, à la même forme de celui-ci, etc.; les résultats ne sont pas les mêmes dans un appareil de silice ou de nickel; de plus, comme nous l'avons reconnu récemment, la thermobalance doit être corrigée de courants de convection pour éviter la „montée du creuset vide". Toutes ces causes d'erreur qui étaient déjà bien étudiées par GUICHARD et ses élèves ne nous avaient pas échappé dès le début de notre étude; c'est pourquoi, tout au long de celle-ci, nous avons beaucoup plus recherché pour un précipité donné, l'existence d'un palier devant nous servir, par voie de comparaison pour effectuer un dosage automatique que la connaissance exacte des températures du début et de la fin puisque, en fin de compte, nous utilisons la température du milieu du palier.

3. Jusqu'en 1949, nous avons utilisé avec la thermobalance Chevenard un mode de chauffage avec rhéostat muni d'un mouvement d'horlogerie et dont les vitesses sont indiquées page 20 du livre *Inorganic Thermogravimetric Analysis*. Depuis cette date, nous avons installé sur nos thermobalances les fours à cycle thermique imposé qui donnent des échauffements linéaires. Comme M. WENDLANDT opère avec un autre mode d'échauffement que nous, ses résultats sont tout aussi acceptables que les nôtres; tout dépend de ce qu'il veut en faire.

4. La courbe de thermolyse du phosphomolybdate d'ammonium réalisée à plusieurs exemplaires en 1946 en s'inspirant des données du traité de TREADWELL a été recommencée ces jours-ci et nous a donné le même résultat en creuset d'aluminite, sur 200 mg et avec la première vitesse de chauffe. Nous maintenons donc nos résultats de 1946.

5. Le spectre d'absorption infrarouge du précipité de phosphomolybdate d'ammonium, même réalisé par la technique de STOCKDALE accuse sans cesse la présence de groupes PO_4 et de groupes MoO_3 à l'exclusion de groupes Mo_3O_{10}, c'est pourquoi, dans nos calculs, nous continuons d'employer la formule habituelle $(NH_4)_3(MoO_3)_{12}PO_4$.

Reçu le 4 août 1958

THE DETERMINATION OF NICKEL, COBALT, IRON AND ZINC IN FERRITES

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Ferrites are soft magnetic materials which are used in computers, television sweep cores, microwave gyrators, etc. The basic material is essentially magnetic iron oxide in which part of the ferrous iron has been replaced with zinc. Attempts have been made to improve the magnetic properties by the addition of other elements. This investigation was undertaken to develop an analytical method which could be used to analyze the base material for total iron and zinc as well as for nickel and cobalt in materials to which they had been added.

The successful application of ion exchange separations to Alnico[1] indicated that an improved method for the analysis of ferrites could be developed by a similar approach. The methods usually used for the separation of iron, nickel, cobalt and zinc are time-consuming and are not suitable for rapid routine work.

EXPERIMENTAL

The investigation of the application of ion exchange resins to the analysis of Alnico[1] showed that an excellent separation of iron, cobalt, and nickel could be attained on a strongly basic anion exchange resin. The data on the adsorption characteristics of zinc in HCl[2] indicated that zinc would remain in the column during the elution of nickel, cobalt, and iron.

Since the separation of mixtures of iron, cobalt and nickel had already been accomplished, the preliminary experimental work was confined to insuring that the zinc would not pass through the column while these elements were being eluted, and to selecting optimum conditions for the elution of zinc.

A previously analyzed sample was used as a standard material in this investigation. A 1-g sample was dissolved in $9N$ HCl and 0.5 ml of 30% H_2O_2 and transferred to a column (1 cm I.D. × 50 cm long) containing 28 g of a 100–150 mesh strongly basic type anion exchange resin. The sample solution was washed into the resin, and the nickel eluted with 80 ml of $9N$ HCl. The cobalt was then eluted with 75 ml of $4N$ HCl and the iron with 100 ml of $0.5N$ HCl. Each fraction was evaporated to dryness and each element determined by the back titration of an excess of EDTA with a standard $0.03M$ copper sulfate solution. The results of these analyses are shown in Table I. The agreement between the values by the ion exchange method and the previous analyses by independent methods indicate that zinc was not passing through the column. In order to confirm this a standard zinc solution was introduced into the column and the quantities of HCl given above were passed through the column. Zinc was not found in any of these fractions.

The elution of zinc by dilute HCl was not attempted because of the strong absorption of zinc chloride complexes even in dilute HCl[2]. Attempts were made to elute zinc with ammonium hydroxide, perchloric acid, and nitric acid. It was possible to elute the zinc with all of these reagents; however, 3*N* nitric acid was most suitable for the subsequent treatment of the zinc fraction. The results for zinc, also given in Table I, were obtained by eluting with 3*N* nitric acid.

TABLE I

Sample No.	*% Ni Present*	*% Ni Found*	*% Co Present*	*% Co Found*	*% Fe Present*	*% Fe Found*	*% Zn Present*	*% Zn Found*
1	8.2	8.33	0.33	0.33	53.3	53.2	10.4	10.7
2	8.2	8.31	0.33	0.33	53.3	53.2	10.4	10.7
3	8.2	8.31	0.33	0.34	53.3	53.3	10.4	10.7
4	8.2	8.33	0.33	0.33	53.3	53.3	10.4	10.7
5	8.2	8.29	0.33	0.34	53.3	53.2	10.4	10.6

PROCEDURE

Dissolve a 1-g sample in 20 ml of 9*N* HCl and 0.5 ml of 30 vol. % hydrogen peroxide. Transfer the solution of the sample to an ion exchange column with 9*N* HCl. Elute the nickel with 80 ml of 9*N* HCl, the cobalt with 75 ml of 4*N* HCl, the iron with 100 ml of 0.5*N* HCl and the zinc with 100 ml of 3*N* nitric acid. Evaporate each fraction to 5–10 ml. Take a suitable portion of each fraction for the EDTA determination.

All four elements were determined in an identical manner as follows:

Add a 5–10 ml excess of EDTA, 10 ml of acetate buffer (pH $\sim$ 4.8), and back titrate with a standard copper solution using PAN [1-(2-pyridylazo)-2-naphthol] as an indicator.

DISCUSSION

The volumes used for elution were suitable for the columns and resin used in this investigation. The application of this procedure with a different column size or a different resin particle size will require somewhat different elution volumes.

The addition of hydrogen peroxide during dissolution is necessary to insure complete oxidation of iron to the ferric condition. Ferrous iron is only slightly absorbed in 9*N* HCl and would contaminate the nickel and cobalt fractions.

After the elution of zinc with nitric acid, 25 ml of water is added before regenerating the column with 9*N* hydrochloric acid. This precaution is taken to diminish the possibility of generating chlorine in the column. Both the elution of zinc with nitric acid and the regeneration of the column with HCl must be completed without allowing the column to stand for an extended period of time (several hours). The generation of chlorine causes gas bubbles to appear in the column, which necessitates removing the resin and refilling the column.

SUMMARY

An anion exchange technique has been developed for the determination of iron, nickel, cobalt and zinc in a ferrite type material. The constituents are separated by utilizing the differences in the adsorption of their chloride complexes on a strongly basic anion exchange resin. Each constituent is determined by the back titration of an excess of EDTA with a standard copper solution, using PAN as an indicator.

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RÉSUMÉ

Une méthode par échange d'anions est proposée pour le dosage du fer, du nickel, du cobalt et du zinc. La séparation est basée sur les adsorptions différentes des chlorures complexes. Chaque constituant est ensuite dosé par titrage indirect de l'EDTA au moyen d'une solution étalon de cuivre.

ZUSAMMENFASSUNG

Es wird eine Trennung und Bestimmung von Eisen, Nickel, Kobalt und Zink mit Hilfe von Jonen-Austauschern und indirekter EDTA Titration mit einer Standard-Kupferlösung beschrieben. Die Trennung beruht auf der unterschiedlichen Adsorption der komplexen Chloride an stark basischem Anionenaustauscher.

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DETERMINATION OF NICKEL IN GOLD–NICKEL ALLOYS

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The determination of nickel in gold–nickel alloys is complicated by the fact that the dioximes usually used for the precipitation of nickel will reduce gold to the metal. In order to avoid a sulfide precipitation for the separation of gold the possibility of using anion exchange as a rapid means of separation was investigated. It has previously been indicated that gold chloro complexes are strongly adsorbed from a hydrochloric acid solution on a strongly basic anion exchange resin whereas nickel exhibits no adsorption in chloride solutions[1,2]. Investigations with synthetic mixtures of nickel and gold showed that nickel is not noticeably retarded in the column while the gold complex is retained at the top of the column in hydrochloric acid solutions from 2 to 12N.

The determination of nickel was concluded by the back titration of an excess of standard EDTA with a standard copper solution[3].

PROCEDURE

Dissolve a sample in aqua regia to give 15 to 50 mg of nickel. Remove the nitric acid by evaporation to dryness several times on a steam bath. Take up the chlorides with 2N HCl and transfer the solution to an ion exchange column (1-cm diameter) containing 5 g of Dowex 1-X8, 100–200 mesh, chloride form. Wash the sample solution down the sides of the column and elute the nickel into a 250-ml beaker with 2N HCl. Neutralize the eluent with 50% potassium hydroxide until a permanent precipitate just forms. Redissolve the precipitate of nickel hydroxide with 0.1N hydrochloric acid. Add a measured excess of standard EDTA (0.03M), 10 ml of a sodium acetate–acetic acid buffer (0.5M sodium acetate–0.5M acetic acid) and sufficient water to give approximately 300 ml of solution. Heat to 70-90°, add 3 to 4 drops of PAN[4,5] and back titrate with a standard copper solution (0.03M). Calculate per cent nickel from the following expression:

$$\%\text{Ni} = \frac{(V_{\text{EDTA}} \times F - V_{\text{Cu}})\, 92.37 M_{\text{Cu}}}{\text{mg of sample}}$$

where V_{EDTA} and V_{Cu} represent the volumes of EDTA and standard copper solution in ml and F represents the volume (in ml) of standard copper whose molarity is M_{Cu} equivalent to 1 ml of EDTA solution.

DISCUSSION

The separation of nickel from gold is simplified by the use of anion exchange resins. The gold(III) chloride complex is adsorbed so strongly by the resin that it is not practical to remove the gold from the column after each sample. Successive samples are separated in the column until the gold complex is within a few centimeters of the bottom of the column as indicated by the bright orange color of the adsorbed complex. The resin is then removed and the column recharged.

The results given in Table I are from a synthetic solution made up of pure gold and nickel.

TABLE I

Sample No.	*Gold added mg*	*Nickel added mg*	*Nickel found mg*	*Error mg*
1	—	19.50	19.54	0.04
2	—	19.50	19.48	0.02
3	—	19.50	19.48	0.02
4	—	19.50	19.50	0.0
5	80	19.50	19.50	0.0
6	80	19.50	19.54	0.04
7	80	19.50	19.59	0.09
8	80	19.50	19.61	0.11
9	80	19.50	19.55	0.05

SUMMARY

An ion exchange separation based on the difference in adsorption from a chloride solution combined with an EDTA titration is suggested as a rapid and accurate method for the determination of nickel in nickel-gold alloys.

RÉSUMÉ

Une séparation par échange d'ions est proposée comme méthode rapide et précise pour le dosage du nickel dans les alliages nickel–or.

ZUSAMMENFASSUNG

Es wird eine schnelle und genaue Methode zur Bestimmung von Nickel in Nickel–Gold Legierungen mit Hilfe von Jonen-Austauschern und einer EDTA Titration beschrieben.

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ELECTROCHROMATOGRAPHY IN THE SEPARATION OF IONS

VII. SEPARATION OF ALKALINE EARTH METALS

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In previous communications to this Journal attempts to separate common elements belonging to the groups occurring in the analytical table have been described. The ions of the silver group[1] separate into distinct zones with a decinormal solution of sodium chloride, potassium chloride or potassium cyanide. The elements of the copper group[2] form separate bands in the presence of potassium chloride. Such a separation into distinct bands also occurs in the case of members of the zinc group[3] in the presence of potassium cyanide at pH 6.0.

The separation of alkaline earth metals from mixtures of two such elements, with metaphosphate as the electrolyte, has recently been reported by MAKI[4], who has also suggested the possibility of separating a ternary mixture, Ca, Ba(Sr) and Mg, with the aid of a mixture of ethylenediamine or triethanolamine and ammonium tartrate. EVANS AND STRAIN[5] have found that citric, tartaric and lactic acids, but not their ammonium salts, are effective for the separation of Ca, Sr and Ba from a mixture.

The investigation of the separation of the ions of the alkaline earth metals, reported here, shows that separation of ternary mixtures of Ca, Mg and Sr or Ba and of a few binary mixtures are quite feasible even when the most common electrolytes such as ammonium nitrate and chloride are used.

EXPERIMENTAL

The solutions of the ions of calcium, magnesium, strontium and barium were prepared from the nitrates; a small drop (0.01 ml) of the mixtures contained about 20 μg of each ion. The electrolytes used were all decinormal in strength. Solutions of sodium rhodizonate ($M/100$) and 8-hydroxyquinoline ($M/10$) were prepared in distilled water and in N acetic acid respectively.

The experimental technique was exactly the same as reported in earlier papers and here also the signs + and — signify migrations towards anode and cathode respectively. In Table I the movements of the ions in cm are recorded.

An attempt was made to carry out those separations that, on the basis of the migration values, appeared to be fairly feasible. Only a few separations, which are reported in Table II, were found to be successful; in a large number of cases the bands fused together due perhaps to some sort of influence exerted by the ions on each other. The square brackets indicate that the ions enclosed have a portion of their migration zone in common although they can easily be detected. Failure to locate the bands is shown in Table I by dashes.

DISCUSSION

From the movements of the ions of the calcium group it is clear that they have a low tendency to complex formation; in a number of cases owing to complex formation or precipitation reactions the chromogenic reagents fail to locate the bands. Only in the presence of sodium citrate are all the four ions anionic while in all other electrolytes they behave as cations.

Separation of barium and strontium from each other with electrolytes such as hydrochloric acid and potassium iodide was found not to be possible, in spite of the quite large difference between the migration values; the bands invariably fused together.

TABLE I

Ions	*HNO_3*	*NH_4NO_3*	*H_3PO_4*	*$HClO_4$*	*HCl*	*NH_4Cl*	*NaCl*	*KCl*	*NaBr*
Mg^{+2}	—3.4	—6.7	–	—5.4	—4.0	—6.1	—11.0	—9.6	—11.0
Ca^{+2}	—3.5	—3.0	—4.7	—5.0	—5.7	—0.5	—13.5	—8.0	—12.3
Sr^{+2}	—6.0	—8.1	—5.5	—6.0	—5.4	—9.0	—10.1	—9.9	—11.8
Ba^{+2}	—5.8	—8.3	—5.8	—6.5	—3.7	—8.5	—10.0	—10.0	—10.9

Ions	*KI*	*CH_3CO_2H*	*NH_4 acetate*	*$NaNO_2$*	*$Na_2S_2O_3$*	*NH_4CNS*	*KCN(aq.)*	*Thiourea (aq.)*
Mg^{+2}	—8.7	—9.2	—9.0	—6.2	—6.0	—7.5	—0.3	—1.7
Ca^{+2}	—9.5	—2.1	—8.2	—3.2	—5.7	—5.6	—0.3	—0.7
Sr^{+2}	—4.2	—17.1	—11.0	—7.5	—5.1	—7.4	—0.4	—8.5
Ba^{+2}	—10.9	—18.4	—11.8	—7.3	—3.7	—6.6	—0.2	—8.5

Ions	*Thiourea (pH 5.8)*	*Thiourea (0.1N HCl)*	*Tartaric acid*	*Citric acid*	*Na K tartrate*	*Na citrate*	*Na rhodizonate (M/100)*	*Oxine (M/10) in N acetic acid*
Mg^{+2}	—8.9	—5.2	—11.7	—8.0	–	+2.6	—2.9	—6.5
Ca^{+2}	—8.0	—2.0	—13.6	–	–	+7.6	—3.0	—8.5
Sr^{+2}	—10.6	—3.5	—7.1	—13.2	—4.5	+1.8	0.0	—1.7
Ba^{+2}	—8.8	—5.5	—6.5	–	—4.6	+2.5	0.0	—1.0

TABLE II

Electrolyte	*Sequence of separation*
HCl	: [Mg, Sr] —; : Ba, Ca—
HNO_3	: Ca, Ba—; : Ca, Sr—; : Mg, Sr—; : Mg, Ba—
NH_4NO_3	: Ca[Mg, Ba]—; : Ca[Mg, Sr]—
CH_3CO_2H	: Ca, Ba—; : Ca, Sr—
NH_4Cl	: Ca, Mg, Sr—; : Ca, Mg, Ba—
NaCl	: Sr, Ca—; : Ba, Ca—; : Mg, Ca—
$NaNO_2$	: Ca, Ba—; : Ca, Mg—; : Ca, Sr—
Thiourea (aq.)	: Ca, Mg—; : Ca, Ba—; : Ca, Sr—
Na rhodizonate or oxine	: Sr, Mg—; : Sr, Ca—; : Ba, Ca—; : Ba, Mg—

SUMMARY

Complete separation of ternary mixtures of Ca, Mg and Sr or Ba ions with ammonium chloride and less complete but detectable separation of the same mixtures with ammonium nitrate have been achieved, as well as a few binary separations of the type Ca–Ba, Ca–Sr, Ca–Mg, Mg–Sr and Mg–Ba.

RÉSUMÉ

Les auteurs ont pu effectuer, par électrochromatographie, des séparations Ca–Mg–Sr (ou Ba) et des séparations binaires: Ca–Ba, Ca–Sr, Ca–Mg, Mg–Sr et Mg–Ba.

ZUSAMMENFASSUNG

Es wird eine elektrochromatographische Methode zur Trennung von Ca, Mg und Sr (oder Ba) sowie die Trennung binärer Gemische von Ca – Ba, Ca – Sr, Ca – Mg, Mg – Sr und Mg – Ba beschrieben.

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DETERMINATION OF Ni, Zn AND Al IN BRONZES AND BRASSES AFTER DETERMINING Cu-Pb-Sn-Sb BY CONTROLLED-POTENTIAL ELECTROLYSIS

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A method for the determination of copper, lead, tin and antimony by controlled-potential electrolysis and the applications of this method to the analysis of some alloys, particularly bronzes and brasses, have been described in previous papers[1-3].

Further investigations have led to the elaboration of a method for the successive determination of nickel, zinc and aluminium using the solution remaining after the electrolytic separation of the four metals mentioned above. The solution is acid because of its hydrochloric acid content, and contains tartaric and succinic acids. Ammonium salts of all three of these acids are present and, if the alloy to be analysed contains antimony, potassium iodide is also present in the solution.

PRINCIPLE OF THE METHOD

Nickel is precipitated by dimethylglyoxime in slightly ammoniacal medium; in the filtrate zinc is separated by controlled-potential electrolysis. The solution is subsequently treated with 8-hydroxyquinoline to separate the aluminium which, after filtration and dissolution of the oxinate, is precipitated with ammonium benzoate.

Reagents (Merck, pro analysi)

Concentrated ammonia, sp.gr. = 0.88.
Dilute ammonia (1 + 1).
Concentrated sulphuric acid, sp.gr. = 1.83.
Concentrated nitric acid, sp.gr. = 1.38.
Dilute nitric acid (1 + 1).
Perchloric acid (60% solution).
Thioglycollic acid (76% solution).
Hydrazine hydrochloride.
Solution of dimethylglyoxime: dissolve 10 g of KOH in 400 ml of distilled water, add 10 g of dimethylglyoxime and stir until solution is complete, then bring to 1 l with distilled water.

Solution of gelatine: dissolve 0.2 g of gelatine in 70 ml of warm distilled water and bring to 100 ml with distilled water.

10% aqueous solution of KCNS.

Solution of 8-hydroxyquinoline: dissolve 2 g of 8-hydroxyquinoline in 70 ml of distilled water containing 6 ml of glacial acetic acid and bring to 100 ml with distilled water.

Solution of ammonium benzoate: dissolve 10 g of ammonium benzoate in 70 ml of warm distilled water and bring to 100 ml with distilled water (if the benzoate precipitates when the solution is cold, heat it before use).

Benzoate wash solution: dissolve 2 g of ammonium benzoate in 170 ml of distilled water, add 4 ml of glacial acetic acid and bring to 200 ml with distilled water.

DETERMINATION OF NICKEL

Neutralize the solution remaining after the determination of copper, lead, tin and antimony, with ammonia until a pH of 6–7 is obtained and add a slight excess of dimethylglyoxime solution; 10 ml are usually sufficient. Then bring the pH to 7.5–8 (check with narrow range test papers) with ammonia while stirring the solution during the precipitation; heat to 45–50°, but not beyond this temperature, set aside for 10–15 minutes and then filter at the pump on a weighed Gooch or sintered glass crucible collecting the filtrate in a tall-form 600 ml beaker, wash with distilled water, dry for two hours at 110°, cool in a desiccator and then weigh:

$$\text{Ni }\% = \frac{\text{weight of the nickel dimethylglyoxime} \times 20.32}{\text{sample weight}}$$

Nickel precipitates equally well if an alcoholic solution of dimethylglyoxime is used, but the presence of alcohol in the filtrate adversely affects the subsequent precipitation of aluminium, the oxinate of which is rather soluble in the presence of alcohol; the precipitation of nickel is not disturbed by the presence of tin and antimony and may be carried out without previously separating these elements.

If the iron present in the solution exceeds 20 mg it is advisable to add some drops of 3% hydrogen peroxide before precipitating the nickel. Before filtration, the solution containing the precipitate must not be heated above 50°, otherwise the subsequent determination of zinc will prove difficult.

DETERMINATION OF ZINC

To the dimethylglyoxime filtrate add 2 g of hydrazine hydrochloride, 20 ml of concentrated ammonia and 10 ml of the gelatine solution, then electrolyse the solution at controlled cathode potential to deposit the zinc. The electric circuit, the electrodes and the apparatus have already been described in a previous paper[1].

The electrolysis of zinc is disturbed by iron which, if present in amounts smaller than 10 mg will partially co-deposit with the zinc, while, if present in greater amounts, will also prevent the complete deposition of the zinc itself. An attempt has been made to overcome these difficulties by complexing the iron with CN^- ions in ammoniacal solution or with F^- ions in a solution either weakly acid or ammoniacal, but no advantage was obtained; zinc deposition in formic acid medium has also not proved satisfactory. Therefore, it is necessary to avoid determining the zinc by electrolysis when the amount of iron exceeds 10 mg, while when the iron present in the solution is less than 10 mg, a determination of the iron co-deposited with zinc must be made.

Zinc deposition is always accompanied by a considerable evolution of hydrogen, and if this evolution ceases it means that the zinc deposition has also ceased.

During the electrolysis the solution assumes a pink or red colour owing to the reaction of the ferrous iron with the dimethylglyoxime previously added for the separation of nickel.

Some manganese dioxide may separate at the anode when the electrolysis is approaching completion; this oxide may be redissolved, if desired, simply by immersing the anode in the electrolyte after the electrolysis is finished and the cathode has been removed.

Zinc is deposited by passing a current through the solution (usually 0.4 to 0.8 A) to which a cathode potential ranging from —1.2 to —1.3 V *vs.* S.C.E. corresponds. The cathode potential has a tendency to become immediately more negative.

If manual apparatus is used for potential control, the cathode potential should be allowed to reach —1.50 to —1.55 V *vs.* S.C.E. during the electrolysis; if potassium iodide is present in the solution it is preferable not to let the cathode potential exceed —1.50 V *vs.* S.C.E.

However, some cases are met with — specially when iron exceeds 3-4 mg — where the cathode potential does not spontaneously become more negative down to —1.45 and —1.50 V *vs.* S.C.E.; it is therefore necessary to lower it first to —1.45 V *vs.* S.C.E. (10-15 min after the electrolysis has started) and then to —1.50 V *vs.* S.C.E. (20-30 min before the electrolysis ends).

If automatic apparatus is used, start the zinc electrolysis with a cathode potential (about —1.2 to —1.3 V *vs.* S.C.E.) to which a current intensity of 0.4-0.8 A corresponds; then gradually raise the cathode potential to —1.5 to —1.55 V *vs.* S.C.E.

The electrolysis takes 50-60 min for bronzes and from 1 h 15 min to 1 h 20 min for brasses; after the electrolysis is finished the zinc deposit is washed with distilled water containing a drop of ammonia per liter and then with alcohol and ether; finally, it is dried at 100° and weighed.

A noticeable amount of the current flowing through the solution is used up by secondary reactions such as the evolution of hydrogen at the cathode and the cyclic oxidation and reduction of iron, at the anode and the cathode respectively. As a consequence, the deposition of the last traces of zinc is slow. Furthermore, when the amount of zinc is less than 10 mg it is not advisable to bring the cathode to a potential more negative than —1.48 to —1.50 V *vs.* S.C.E. because the only result would be an increased evolution of gas.

When the electrolyte contains potassium iodide (added if antimony has been previously determined) and the amount of iron is less than about 3 mg, the cathode potential must not be adjusted to values more negative than —1.48 to —1.50 V *vs.* S.C.E., because otherwise a rise in the anodic potential will also occur, causing the separation of iodine, which partially clings to the zinc deposit; this then assumes a blackish appearance. However, if the iron present in the solution exceeds 3 mg, this will prevent the separation of iodine even if the cathode is more negative than —1.50 V *vs.* S.C.E.

If the amount of iron present in the solution is greater than 9-10 mg, then the deposition of zinc is incomplete in any case; this limitation restricts the possible applications of the method, but, in the numerous cases in which it is applicable, the results agree with those obtained with methods that are more complex and time-consuming. Table I shows the results of the determinations carried out on seven samples of known composition; the range of their compositions covers the more usual cases met with in current analysis, excepting those alloys that contain more than 1% of iron.

To evaluate the iron co-deposited with the zinc (from a few tenths to 30-40 tenths of a mg, depending on the total amount of iron present in the electrolyte) several methods may be followed; the method used by the author is as follows[4]: dissolve the zinc deposit in 15 ml of lukewarm HNO_3 (1+1), boil and bring to 250 ml; transfer 25 ml of the solution to a 100-ml flask, heat at approximately 50°, add 10 ml of the KCNS solution, let stand for 1 min, cool to 20°, bring to volume and take a photometric measurement against distilled water (check that reagents and vessels are free from iron). A Pulfrich photometer, 546 Hg filter, was used. The percentage of iron so found is subtracted from that of zinc.

$$\text{Fe}\ \% = 1.518\ k\ (\text{for 1 g sample})$$

$$k = \text{extinction coefficient}$$

DETERMINATION OF ALUMINIUM

The aluminium possibly present in the solution remaining after the zinc electrolysis may be separated by means of hydroxyquinoline. If the zinc deposition was not quantitative, owing to the presence of too large an amount of iron, this does not affect the determination of aluminium.

The hydroxyquinoline also precipitates the iron and most of the manganese; in the presence of potassium cyanide the co-precipitation of these two elements is prevented, but if manganese is present in amounts greater than 5 mg, manganese ferrocyanide will separate, which is very difficult to filter. Also if manganese is absent, or present in amounts of not more than 5 mg, the precipitation of pure aluminium oxinate of stoichiometric composition requires some special conditions[5], which cannot be applied to this particular test-solution. Therefore the hydroxyquinoline is used for a preliminary separation, while the quantitative determination of aluminium is carried out by precipitation with ammonium benzoate.

Heat the solution from which zinc has been separated to 60° and do not exceed 70°. While continuously stirring, add drop by drop an excess of the hydroxyquinoline solution; at least 1 ml of the precipitating solution is required for every mg of aluminium, iron and manganese; it is always inadvisable to use less than a total of 15 ml. Allow to cool, filter on Whatman No. 40 paper and wash with distilled water. (If it is desired to prevent the co-precipitation of iron, add 3 g of potassium cyanide to the solution before heating to 60°.)

Transfer both the filter and the precipitate to the beaker in which the precipitation has been carried out and add 10 ml of conc. sulphuric acid; let the paper carbonize, add 10 ml of conc. nitric acid, cover with a watch glass and heat until all nitrous vapors are eliminated. Remove the watch glass and bring to sulphuric acid fumes; take the beaker off the plate, add 3 ml of perchloric acid and then bring to perchloric acid and subsequently sulphuric acid fumes.

Allow to cool, dilute with distilled water to approximately 70 ml, boil to dissolve the aluminium sulphate and allow to cool.

TABLE I

RESULTS OF THE ANALYSES OF SAMPLES WITH KNOWN COMPOSITION

Sample		*Values found* *				
		1	*2*	*3*	*4*	*5*
N. 207 Bronze C (B.Ch.S.)	Cu	86.82	86.72	86.64	86.73	86.88
Cu = 89.65–87.00; Ni = 0.09	Pb	0.36	0.41	0.38	0.38	0.38
Pb = 0.41; Zn = 2.53; Fe = 0.06	Sn	9.82	9.80	9.92	9.80	9.74
Sn = 9.71–9.97; Ag = 0.02	Sb	n.d.	n.d.	n.d.	n.d.	n.d.
Sb = 0.04; As = 0.05; S = 0.005	Ni	0.11	0.08	0.07	0.10	0.09
	Zn	2.54	2.52	2.55	2.59	2.53
Al added: to 2 = 0.20%; to 3 = 0.10%	Al	—	0.18	0.095	—	—
N. 52 c Cast Bronze (N.B.S.)	Cu	89.26	89.21	89.22	89.21	89.26
Cu = 89.25; Ni = 0.76; S = 0.002	Pb	n.d.	n.d.	n.d.	n.d.	n.d.
Pb = 0.011; Zn = 2.12; P = 0.001	Sn	7.77	7.81	7.76	7.78	7.79
Sn = 7.85; Fe = 0.004	Ni	0.75	0.77	0.78	0.78	0.75
	Zn	2.12	2.10	2.15	2.10	2.14
Al added: to 2 = 0.50%; to 3 = 0.30%	Al	—	0.49	0.28	—	—
N. 63 b Phosphor Bronze (N.B.S.)	Cu	77.88	77.92	77.89	77.88	77.87
Cu = 77.94; Ni = 0.33; P = 0.44	Pb	9.27	9.26	9.28	9.25	9.35
Pb = 9.36; Zn = 0.71; S = 0.16	Sn	9.77	9.76	9.81	9.76	9.78
Sn = 9.78; Fe = 0.47; Ag = 0.04	Sb	0.50	0.52	0.48	0.46	0.49
Sb = 0.54; Si = 0.12; Al = 0.05	Ni	0.33	0.34	0.32	0.30	0.36
	Zn	0.67	0.75	0.74	0.70	0.73
Al added: to 3 = 0.50%; to 4 = 0.20%	Al	n.d.	n.d.	0.54	0.24	n.d.
N. 124 c Ounce Metal (N.B.S.)	Cu	84.21	84.18	84.18	84.17	84.19
Cu = 84.22; Ni = 0.60; S = 0.048	Pb	4.70	4.70	4.68	4.69	4.78
Pb = 4.74; Zn = 4.93; P = 0.024	Sn	5.10	5.12	5.12	5.07	5.07
Sn = 5.13; Fe = 0.107	Sb	0.18	0.20	0.20	0.19	0.18
Sb = 0.20; Si = 0.002	Ni	0.58	0.59	0.60	0.57	0.61
	Zn	5.01	5.02	4.94	4.99	4.91
Al added: to 3 = 0.10%; to 4 = 0.20%	Al	—	—	0.10	0.21	—
N. 37 d Sheet Brass (N.B.S.)	Cu	70.79	70.72	70.79	70.85	70.76
Cu = 70.78; Ni = 0.58	Pb	0.92	0.93	0.87	0.94	0.93
Pb = 0.94; Zn = 26.65	Sn	0.94	0.95	0.95	0.95	0.92
Sn = 0.97; Fe = 0.076	Ni	0.57	0.59	0.57	0.55	0.60
	Zn	26.68	26.65	26.66	26.67	26.70
Al added: to 3 = 0.30%; to 4 = 0.50%	Al	—	—	0.28	0.52	—
N. 62 b Manganese Bronze (N.B.S.)	Cu	57.45	57.40	57.38	57.37	57.43
Cu = 57.39; Ni = 0.27; Mn = 1.29	Pb	0.23	0.24	0.22	0.25	0.22
Pb = 0.28; Zn = 37.97; Si = 0.048	Sn	0.89	0.87	0.88	0.92	0.92
Sn = 0.96; Al = 0.97; As = 0.004	Ni	0.24	0.25	0.28	0.27	0.30
Sb = 0.005; Fe = 0.82; Ag = 0.005	Zn	37.92	37.88	38.03	37.90	37.96
	Al	0.95	0.94	0.95	0.92	0.99
N. 62 c Manganese Bronze (N.B.S.)	Cu	59.18	59.19	59.16	59.17	59.14
Cu = 59.16; Zn = 37.24	Pb	0.20	0.18	0.18	0.25	0.22
Pb = 0.24; Al = 1.22	Sn	0.37	0.36	0.37	0.35	0.37
Sn = 0.39; Fe = 0.74	Ni	0.27	0.27	0.27	0.29	0.31
Ni = 0.28; Mn = 0.66	Zn	37.24	37.19	37.26	37.20	37.27
Si = 0.068	Al	1.21**	1.21	1.23**	1.22	1.26

* n.d. = not determined.

** Al precipitated with 8-hydroxyquinoline in the presence of KCN.

A possible violet colour is due to the presence of manganese oxidized to permanganate by the perchloric acid; this coloration is eliminated with some hydrazine hydrochloride or sulphate.

Filter to separate the silica which, though almost invisible, is always present; wash the filter with distilled water. Add 2 ml of thioglycollic acid to the filtrate, heat and add little by little while stirring 20 ml of the ammonium benzoate solution and then neutralize first with conc. ammonia and subsequently with dilute ammonia to pH 3.6–4.2. If necessary, correct with dilute sulphuric acid and ammonia (check with narrow range pH test papers or use bromophenol blue as indicator). Heat and boil for a few minutes while stirring the solution occasionally. Allow to settle, filter on Whatman No. 40 paper, wash with warm benzoate wash solution, ignite and weigh.

$$\text{Al}\ \% = \frac{\text{weight of } Al_2O_3 \times 52.91}{\text{sample weight}}$$

In Table I the results obtained in the analysis of some samples of known composition are listed; copper, lead, tin and antimony were determined according to the method described in previous papers[1,2] and nickel, zinc and aluminium according to the method described here. Besides supporting the method outlined here, the values found are a further confirmation of the suitability of the method previously described.

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SUMMARY

A method is given, which allows nickel, zinc and aluminium to be determined in the solution remaining after the determination of copper, lead, tin and antimony by controlled-potential electrolysis. Nickel is precipitated by dimethylglyoxime, zinc is deposited by controlled-potential electrolysis and aluminium is precipitated first by oxine and then by ammonium benzoate.

RÉSUMÉ

Une méthode est proposée pour le dosage du nickel, du zinc et de l'aluminium dans la solution résultant du dosage du cuivre, du plomb, de l'étain et de l'antimoine par électrolyse à potentiel contrôlé.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von Nickel, Zink und Aluminium in einer Lösung, die nach der Bestimmung von Kupfer, Blei, Zinn und Antimon mittels Elektrolyse bei kontrolliertem Potential übrig bleibt.

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PRECISION NULL-POINT POTENTIOMETRY

A SIMPLE, RAPID AND ACCURATE METHOD FOR LOW CONCENTRATION CHLORIDE DETERMINATIONS

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Chloride determinations have been performed by a variety of methods, but the most generally used are the titration methods, using visual, potentiometric, amperometric and other end-point detection systems. The titration procedure is capable of good accuracy except when the chloride concentrations are too low. At low chloride concentrations, absolute potential measurements in a concentration cell containing two silver–silver chloride electrodes can yield satisfactory quantitative results as demonstrated by FURMAN AND LOW[1,2] and others[3,4]. This method is rapid and provides good chloride results if the equipment is properly set up and all samples adjusted to about the same over-all ionic strength.

Unfortunately, with the regular concentration cell method it is necessary to maintain the reference and samples at the same and constant known temperature, and this requires an inconvenient temperature controlling system. Also, in dilute chloride solutions it is necessary to correct for chloride contribution by the Ag–AgCl electrode solubility and for the chloride content of any reagents used. These calculations can be quite time-consuming, and even with care the relative accuracy is seldom better than 1%, regardless of the concentration range. The accuracy by the regular concentration cell method is better than obtainable by the titration procedure for dilute solutions (about $10^{-4}M$ and below), but less for the higher concentrations, where 0.1% relative accuracy is often possible by the titration method.

In order to eliminate the difficulties inherent in the regular concentration cell method and readily provide results of better accuracy, a new technique was developed which is herein referred to as Precision Null-Point Potentiometry. The new method can be applied for determinations of chloride over a wide concentration range, as low as $10^{-6}M$ and as high as necessary if the sample can be diluted to at least $0.1M$. The method does not require a temperature controlling system, and calculation corrections are not necessary for electrode solubility and chloride contributions by reagent impurities. The only calculation necessary for determining chloride concentration is either a simple addition or subtraction of two numbers. The method is especially applicable where the chloride concentrations for a series of samples vary over a relatively small range. In this case, even though the chloride concentration is sufficiently high so that a titration would be satisfactory, the precision null-point potentiometric method can be more rapid and accurate. For example, the chloride concentration of a prepared solution sample could be determined in less than a minute with an accuracy of 0.1%, and sample preparation for some samples would require only a few seconds.

The precision null-point potentiometric method consists simply of changing the chloride concentration of the unknown solution, while maintaining the ionic strength constant, until it is of identical concentration to a known reference solution. This can be accomplished experimentally in such a way that temperature control and calculation corrections are not necessary. The general principles and simple experimental techniques are described and results for chloride presented.

GENERAL PRINCIPLES OF THE METHOD

If the liquid junction potential of a concentration cell is negligible, which is the case if the ionic strength is the same on both sides of the junction, then the e.m.f. of the cell is given by equation (1),

$$E = kT \log \frac{a_u}{a_R} = kT \log \frac{C_u}{C_R} + kT \log \frac{\nu_u}{\nu_R} \quad \ldots\ldots\ldots\ldots \quad (1)$$

where a_u, C_u, ν_u and a_R, C_R, ν_R are the activity, concentration and activity coefficient for the potential determining species in the unknown and reference solutions, respectively. It is already assumed that the ionic strengths in both solutions are essentially equal so the activity coefficients are equal and the second term of equation (1) drops out and

$$\frac{C_u}{C_R} = 10^{E/kT} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Since the method to be described has been used for the determination of chloride, the following discussion and equations will refer to chloride specifically, but the method is general and should be applicable for other determinations.

Assume the following conditions: (a) It is possible to set up a concentration cell, as shown in Fig. 1, consisting of an unknown chloride solution in a beaker and a chloride reference solution in a small glass isolation compartment which provides electrical contact but prevents any significant mixing of the two solutions; (b) there is zero or a small constant potential across the electrode pair when the solutions in the isolation compartment and beaker are the same concentration; (c) a pair of Ag–AgCl electrodes having nearly identical characteristics is available, with one placed in the reference and the other in the unknown solution; (d) the chloride concentration of the unknown can be easily and rapidly changed by either dilution or addition of a more concentrated standard chloride solution while maintaining the ionic strength of the unknown equal to the reference solution and stirring the unknown solution continuously with a motor-driven paddle stirrer; (e) both reference and unknown solutions rapidly come to the same temperature under experimental conditions.

Under these conditions it is apparent from equation (2) that when $E = 0$ the concentrations of the adjusted unknown solution, C_{uA}, and the reference solution, C_R, are the same, *i.e.*,

$$C_{uA} = C_R \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

and independent of the temperature. The procedure consists simply of changing the original volume, V_o, of unknown chloride solution of concentration C_u, until the null potential is reached, at which point the solution has a new total volume $(V_o + V_a)$ and a concentration equal to the known reference C_R.

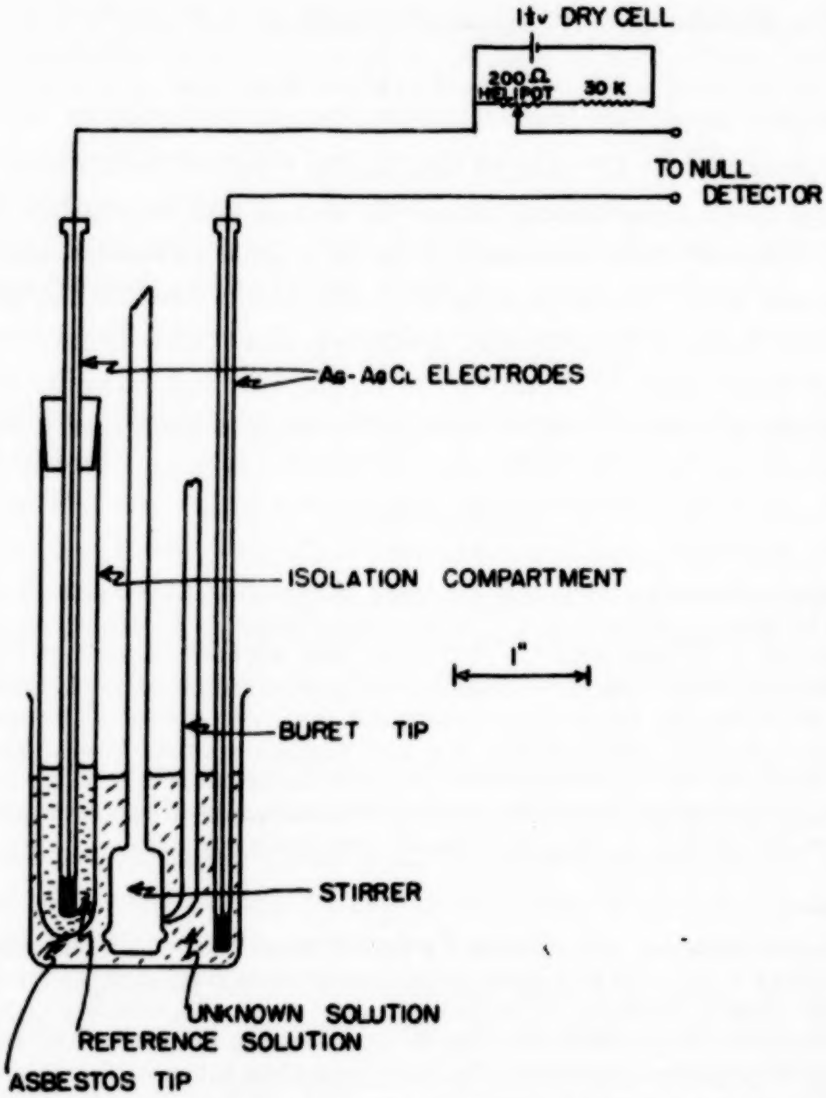
1½v DRY CELL
200 Ω HELIPOT
30 K
TO NULL DETECTOR
Ag-AgCl ELECTRODES
ISOLATION COMPARTMENT
1"
BURET TIP
STIRRER
UNKNOWN SOLUTION
REFERENCE SOLUTION
ASBESTOS TIP

Fig. 1. Precision null-point potentiometric apparatus for chloride determinations.

If the original unknown solution is diluted by adding a volume, V_a, of a solution containing no chloride, but of essentially the same electrolyte concentration as the reference, then at the null point the quantity of chloride in the unknown, Q_u, is given by equation (4),

$$Q_u = C_R(V_o + V_a) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

If C_R is some exact fraction or multiple of ten, the unknown quantity of chloride, Q_u, can be calculated by adding two numbers, the volume of the original sample aliquot plus the volume of electrolyte added from the buret, and moving the decimal point in accordance with C_R.

If the unknown chloride solution is originally more dilute than the reference, it is made more concentrated by adding a chloride solution more concentrated than the reference, for example, exactly $2C_R$. In this case at the null point the total quantity of chloride present in a volume $(V_o + V_a)$ is the sum of the chloride in the unknown, Q_u, and the quantity added, Q_A, and

$$\frac{Q_u + Q_A}{V_o + V_a} = C_R \quad \quad (5)$$

Since $Q_A = 2C_R V_a$, it follows from equation (5) that,

$$Q_u = C_R(V_o - V_a) \quad \quad (6)$$

Although it is assumed in the above discussion that no chloride is contributed by the electrolyte and other reagents or the electrodes, it can be readily shown that such contributions of chloride will not enter into the final calculations if the reference solution is made up with the same reagents and same concentration as for the unknown samples and both reference and unknown electrodes have similar characteristics. This is generally easy to attain in practice, but too large a chloride contribution by the reagents and electrodes obviously decreases sensitivity of null detection.

APPARATUS

Electrodes

The Ag–AgCl electrodes were prepared by using the plating procedure of BROWN AND MACINNES[5] and the chloridizing procedure of FIANDA AND NAGEL[6]. Platinum plate electrodes (2 × 1/2 cm, 1 × 1/2 cm, 1/2 × 1/2 cm, and 1/2 × 1/5 cm) and wire electrodes, (1 cm long and 1 mm diameter) were used. All electrodes were plated and chloridized in pairs. It was possible to easily prepare electrode pairs having asymmetry potentials, *i.e.*, the potential between two electrodes in the same reference solution, less than 0.1 mV, and negligible drift. These electrodes were stable for months when kept in the reference solution and never allowed to dry out. The potential between the two electrodes when in solutions of same concentration and separated by the isolation compartment, as shown in Fig. 1, was also usually less than 0.1 mV.

Isolation compartment

Several methods for isolating the reference solution were found satisfactory and are referred to as the asbestos fiber type, cracked glass type, and porous unglazed vycor type. The asbestos fiber type was made from a Beckman fiber type calomel electrode, number 4970, by cutting away the plastic cap and cleaning the tube thoroughly and soaking for several hours in distilled water to remove all traces of potassium chloride. The tube was then filled with the appropriate reference solution and after about an hour was ready for use. The cracked glass type was made by sealing a bead of soft glass in a small hole in the bottom of a pyrex test tube. As the soft glass cooled it produced many small cracks providing electrical contact, but preventing any significant mixing of reference and unknown solutions. The cracked glass type usually has a larger electrical resistance than the asbestos fiber type. The unglazed vycor type, which is made from Corning porous glass 7930 and described by CARSON *et al.*[7] has a lower resistance than the other two types and prevents mixing of the two solutions. However, it must be filled with reference solution for at least one day before it can be used.

Stirring equipment

The stirrer setup for the Sargent-Malmstadt automatic titrator[8] was used to assure efficient stirring and to provide a means of holding the beaker and isolation compartment and of allowing a simple and rapid changing of beakers. To obtain the most efficient mixing of the solution being added by the buret and the solution in the beaker, the buret tip is pointed at and nearly in contact with the enlarged end of the Sargent stirrer as shown in Fig. 1. The electrode outside the isolation compartment is held firmly in place by means of one of the clips on the side of the Sargent-Malmstadt titrator stand. The isolation compartment is held in place by the other clip, and the electrode inside the compartment is held in place by means of a split one-holed cork which fits into the tube as shown in Fig. 1.

Zero-suppress

In order to use zero as the null potential, it was necessary to buck out the small potential between the electrodes when the solution in the beaker was the same concentration as that in the isolation compartment. This was accomplished by using a ten-turn Helipot in series with a resistor across a 1.5 V dry cell so that a 0 to 10 mV bucking voltage could be applied. However, if more than 1 mV exists across the electrodes in the above case, something is probably wrong, and the system should be checked.

Null detector

For expediency in studying the characteristics of the system, a Leeds and Northrup 10 mV Speedomax recording potentiometer was used as the null detector. Other types of null detectors could be used, the sensitivity depending on the required precision. Systems for automatically terminating the addition of reagent at the null potential could also be easily applied.

Burets

Fischer-Porter automatic self-zeroing, 25 ml, precision-bore, teflon stopcock burets were used for adding the reagent. Each buret was filled through a sidearm fitted with a teflon stopcock connected to a large reservoir of appropriate reagent.

PREPARATION OF SOLUTIONS

The most suitable chloride concentration for the reference depends on the concentration range of chloride in the unknowns, and the reference is made up so that the final chloride results can be obtained in suitable units, such as milliequivalents, parts-per-million, or per-cent, by simple addition or subtraction of volume of reagent added from the buret and volume of sample aliquot or some multiple of it. The reference solutions, solutions added, and unknown solutions used for the experimental work were $1.000 \cdot 10^{-2}$ to $1.000 \cdot 10^{-6}M$ chloride made from reagent grade sodium chloride.

The ionic strength of different unknown samples might vary considerably, and since it is necessary that all samples and reference solution have essentially the same ionic strength, it is desirable to add a large known quantity of electrolyte to all solutions so that the contribution to the ionic strength of ionic constituents in the sample is insignificant. Of course, at the null point the chloride contribution to the ionic strength is the same in both solutions. All solutions used for the experimental work described herein were prepared to be 1*M* sulfuric acid, by pipetting suitable aliquots of 5 or 10*M* sulfuric acid and diluting to correct volume. To assure that the same amount of chloride is added to all solutions by the H_2SO_4, a large volume (20 l) of 5 or 10*M* H_2SO_4 was prepared and used in making the reference and in preparing samples for analysis.

Although the chloride concentration from the added electrolyte does not enter into the final calculation, since it is the same in the reference and unknown solutions, it is desirable to use an electrolyte containing a very small amount of chloride to prevent a decrease in sensitivity of null detection. This becomes important when the chloride contribution from the electrolyte is large compared to the chloride contribution from the unknown. For this reason sulfuric or nitric acids are good to use because of their commercial availability with low chloride content.

PROCEDURE

Establishment of null point

At the beginning of each day the isolation compartment is emptied and filled to at least a few millimeters above the top of the Ag-AgCl plate with fresh reference solution. The isolation compartment is positioned in the beaker as shown in Fig. 1;

the reference solution is also placed into the beaker and the stirrer started. In order to have a null point at zero, any small potential between the electrodes is bucked out by means of the zero-suppress control. About every hour or two it is a good idea to recheck the null point using reference solution in the beaker and readjusting to zero by means of the zero-suppress. Usually it has not varied by more than ± 0.05 mV upon rechecking unless some unexpected interference fouled the electrodes.

Determination of the unknowns

After setting the null point, the reference solution in the beaker is removed, and the beaker lip is touched to the bottom of the stirrer and isolation compartment to remove the adhering solution. A measured aliquot of the unknown chloride solution is pipetted into a clean, dry, tall-form beaker and the stirrer is started. For example, a 20-ml aliquot is added to a 50-ml beaker, or a 50-ml aliquot to a 100-ml beaker. If the unknown solution is more concentrated in chloride than the selected reference solution, the unknown is diluted by adding $1M$ H_2SO_4 containing no added chloride. This reagent is added at a rate of about 15 ml/min from a teflon stopcock buret with vigorous stirring until the null point is reached. Because a pair of electrodes may not respond instantaneously, about five to thirty seconds are allowed for equilibration, and the addition of reagent is continued if necessary to establish the null point. The buret reading is recorded and the quantity of chloride is expressed in appropriate units as given by equation (4). The entire determination requires from about a few seconds to 2 minutes depending on the volume added.

If the unknown solution is less concentrated in chloride than the selected reference solution, a solution exactly twice the chloride concentration of the reference solution is added from a teflon stopcock buret until the null point is reached. Again five to thirty seconds are allowed for equilibration, and the addition of reagent is continued if necessary to re-establish the null point. The buret reading is recorded, and the quantity of chloride is calculated by equation (6).

After each determination the beaker rim is touched to the bottom of the stirrer and isolation compartment to remove adhering solution. Another beaker containing a new aliquot of chloride is put into place, and the determination is carried out as above.

RESULTS

Several thousand samples were determined having chloride concentrations both larger and smaller than the reference solution. Table I shows results for a typical series of ten identical samples which were twice the chloride concentration of the $1.000 \cdot 10^{-4}M$ chloride reference solution, and required the addition of about 20 ml of sulfuric acid electrolyte reagent to dilute the 20 ml samples to the null point. Similar results were obtained using the asbestos fiber or cracked glass isolation compartments, but the results were not quite as good with the unglazed vycor compartment. Results of equal precision and accuracy were obtained using various sizes and shapes of electrodes, and other samples requiring up to a two-fold dilution.

Results for a typical series of 10 indentical samples which were 10 times more dilute than the reference are shown in Table II. In this case the reagent added is exactly twice the chloride concentration of the $1.000 \cdot 10^{-4}M$ chloride reference solution, and about 18 ml of reagent are added to each 20-ml aliquot of sample to

TABLE I

DETERMINATION OF CHLORIDE BY THE PRECISION NULL-POINT POTENTIOMETRIC METHOD FOR A SAMPLE TWICE THE REFERENCE CONCENTRATION

Millimoles chloride taken	*Millimoles chloride found*	*Deviation*
0.004000	0.004000	0.000000
0.004000	0.004000	0.000000
0.004000	0.003998	0.000002
0.004000	0.003997	0.000003
0.004000	0.004004	0.000004
0.004000	0.004000	0.000000
0.004000	0.003997	0.000003
0.004000	0.003998	0.000002
0.004000	0.003994	0.000006
0.004000	0.003999	0.000001
Ave. 0.004000	0.003999	0.000002

Coefficient of variation: 0.07%

TABLE II

DETERMINATION OF CHLORIDE BY THE PRECISION NULL-POINT POTENTIOMETRIC METHOD FOR A SAMPLE ONE-TENTH THE REFERENCE CONCENTRATION

Millimoles chloride taken	*Millimoles chloride found*	*Deviation*
0.000200	0.000195	0.000003
0.000200	0.000200	0.000002
0.000200	0.000197	0.000001
0.000200	0.000200	0.000002
0.000200	0.000201	0.000003
0.000200	0.000194	0.000004
0.000200	0.000198	0.000000
0.000200	0.000195	0.000003
0.000200	0.000196	0.000002
0.000200	0.000200	0.000002
Ave. 0.000200	0.000198	0.000002

Coefficient of variation: 1.3%

reach the null point. The buret reading error in this case is relatively large compared to the volume difference ($V_o - V_a$), and the relative deviation is considerably larger than for the results shown in Table I. However, it is possible to cover a greater concentration range by the addition of chloride to the sample than by dilution of the sample. Results would, of course, be better with a more precise buret.

Many results were also obtained for even smaller quantities of chloride than those illustrated in Tables I and II. For example, a series of ten identical samples containing 0.100 parts per million chloride was determined with a standard deviation of 0.002 p.p.m. using a 1-p.p.m. reference solution.

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DISCUSSION OF RESULTS

Because of the size of the beaker, only a two-fold range of concentration can be covered when determining an unknown chloride solution by dilution with 1 M H_2SO_4 containing no added chloride, but a ten-fold range of concentration can be covered with good precision and accuracy when determining an unknown solution by addition of a solution twice as concentrated in chloride as the reference solution and 1 M in sulfuric acid. It is possible to cover greater than a ten-fold range with the same reference, but the relative precision of results is more than 1% because of the buret reading errors, as can be seen from equation (6) and the results in Table II. Therefore, it is advisable to either change the reference solution or sample preparation method so that the unknowns and reference do not vary in concentration by more than ten-fold.

The temperature of some reference samples was raised several degrees above the reference solution in the isolation compartment and the samples then placed into position for measurement to determine the time required for reference and unknown solutions to reach the same value and the potential to reach the null point. The time required to equilibrate to within 0.1 mV of the null potential was about 1 min for a 3° change in temperature. Therefore, the sample and reference solutions are essentially at the same temperature by the time the addition of reagent is completed. This, of course, fulfills one of the basic requirements of the method as stated in the initial assumptions. It is important, of course, for rapid temperature equilibrium that the height of reference solution in the isolation compartment be not much above the height of the solution in the beaker.

The effect of ionic strength was also tested, and it was determined that a 1% difference in ionic strength between samples and reference solution caused about a 0.1-mV shift of the null potential. Therefore, the ionic strength in samples and reference solutions must be carefully controlled, but this is easily accomplished using large quantities of electrolyte pipetted accurately as previously described.

Interferences were not studied in detail, but appear to be the same as previously investigated for the absolute potentiometric method for chloride[1-4]. Again, the only abnormal divergence from predicted behavior is brought about by bromide which causes a drifting of the electrode when present in even small concentrations, such as 0.02 p.p.m. In fact, a drifting of electrode potential is a good indication that bromide is present. Errors caused by the slow drifting of electrode potential due to the presence of small bromide concentrations can be overcome by frequent checking and re-establishment of the null point with reference chloride solution.

ACKNOWLEDGEMENT

The authors wish to thank Mr. THEMISTOCLES HADJIIOANNOU for help in making the Ag–AgCl electrodes.

SUMMARY

A new, rapid and accurate potentiometric technique is described for the determination of chloride in the concentration range 10^{-6} to 10^{-1} M. For many samples results can be obtained in less than a minute with 0.1% accuracy. The method consists simply of changing the chloride concentration of an unknown solution, while maintaining the ionic strength constant, until it is of identical concentration to a known reference solution. This can be accomplished experimentally in such a way that temperature control and calculation corrections for chloride from reagents or

electrodes are not necessary. The procedure can be set up so that the calculation for the result is merely an addition or subtraction of two numbers. The general principles and simple experimental techniques are described and results for chloride presented.

RÉSUMÉ

Une nouvelle technique potentiométrique est proposée pour le dosage des chlorures (10^{-6} à $10^{-1}M$). Cette méthode consiste simplement à faire varier la concentration en chlorure de la solution à analyser pour arriver à une concentration identique à celle de la solution de référence, tout en maintenant la force ionique constante.

ZUSAMMENFASSUNG

Es wird eine neue potentiometrische Methode zur Bestimmung von Chlorid im Konzentrationsbereich von 10^{-6} bis $10^{-1}M$ beschrieben. In der zu untersuchenden Lösung wird die Chlorid-Konzentration unter Konstanthaltung der ionischen Stärke der Lösung so variiert, bis sie mit derjenigen einer Referenz-Lösung identisch ist.

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CONFORMATION ET CINÉTIQUE D'OXYDATION DES α,β-AMINO-ALCOOLS ALIPHATIQUES DIASTÉRÉOISOMÈRES

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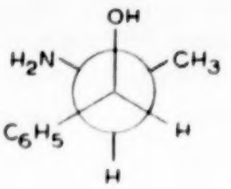
CRIEGEE a montré que le clivage tétracétique des *α,β-glycols* était fortement influencé par la distance séparant les deux groupes fonctionnels. Dans le cas des cyclane-diols[1-4], bien que le mécanisme intime soit encore discuté, la coupure est plus rapide pour la forme *cis* que pour la forme *trans*. Il en est de même pour les aminocyclanols[5].

En série linéaire, CRIEGEE a également observé une notable différence de réactivité entre des diols diastéréoisomères *dl* et *méso*[2-4] que l'on peut attribuer, comme précédemment, à une variation de la distance entre les hydroxyles. On sait, en effet, que la rotation entre les atomes de carbone n'est pas entièrement libre et qu'il existe pour les structures linéaires des conformations privilégiées[6]. Dans la conformation favorisée où les radicaux les plus volumineux sont opposés, les groupes fonctionnels se trouvent rapprochés en série *thréo* ou *dl* et éloignés en série *érythro* ou *méso*.

Nous avons tenté de distinguer les *α,β-amino-alcools* aliphatiques diastéréoisomères par clivage tétracétique. On avait déjà observé une différence entre les formes *thréo* et *érythro* de ces composés lors de la mesure des vitesses de la migration des acyles de l'azote à l'oxygène. La transformation est alors plus rapide pour la *pseudo*-noréphédrine (*thréo*), I, que pour la noréphédrine (*érythro*), II[7–13].



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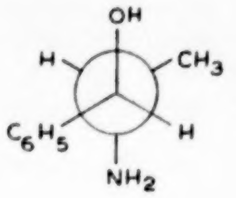

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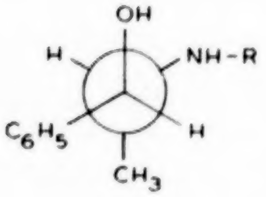

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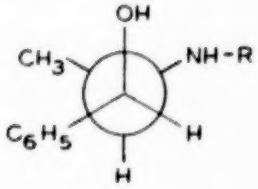

IV

L'emploi du clivage tétracétique offre l'avantage d'une prise d'essai réduite en amino-alcool car il est possible de doser par voie spectrographique le sel de plomb tétravalent non consommé. Celui-ci, contrairement à l'acétate divalent, offre en effet un spectre d'absorption continu entre 2,500 et 3,000 Å. L'oxydation par le réactif tétracétique s'effectue selon le schéma (a) pour les amines β-hydroxylées et selon le schéma (b) pour les amines β,β'-dihydroxylées.

$$\text{(a) R-CHOH-CH(NH}_2\text{)-R}'' \xrightarrow{1/2\,O_2} \text{R-CHO} + \text{R}''\text{-CHO} + NH_3$$

$$\text{(b) R-CHOH-CH(NH}_2\text{)-CH}_2\text{OH} \xrightarrow{O_2} \text{R-CHO} + \text{HCHO} + \text{HCOOH} + NH_3$$

Dans les conditions opératoires ci-après décrites, les différences d'oxydabilité entre la thréonine (*thréo*) et *l'allo*-thréonine (*érythro*) sont confirmées, la forme

TABLEAU I

VITESSE D'OXYDATION D'α,β-AMINO-ALCOOLS DIASTÉRÉOISOMÈRES PAR LE TÉTRACÉTATE DE PLOMB

	Oxygène consommé (en atomes par molécule d'amino-alcool)							
Temps de contact	*Thréonine*	*Allo-thréonine*	*Pseudo-noréphédrine*	*Noréphédrine*	*1-Phényl 2-amino propane 1,3-diol*		*1-p-Nitrophényl 2-amino propane 1,3-diol*	
	(Thréo)	*(Erythro)*	*(Thréo)*	*(Erythro)*	*(Thréo)*	*(Erythro)*	*(Thréo)*	*(Erythro)*
30 minutes			0.73	0.38				
1 heure			0.86	0.52	1.27	0.10	0.80	0.20
2 heures	1.31	0.19	0.98	0.86	1.55	0.14		
3 heures	1.59	0.32	1.00	1.06	1.80	0.17	1.50	0.32
4 heures	1.80	0.45			1.94	0.19		
5 heures	2.0	0.51			2.10		1.83	0.45
6 heures	2.0	0.65						
7 heures	2.1	0.79						

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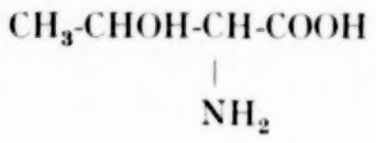
thréo étant oxydée plus rapidement[14]. La valeur stoechiométrique (schéma a) est atteinte pour la thréonine en 15 minutes. La quantité d'oxydant consommée augmente ensuite dans le temps par suite de l'oxydation de l'acide glyoxylique formé pour atteindre 2 atomes d'oxygène par molécule après une heure. L'*allo*-thréonine, oxydée beaucoup plus lentement, consomme respectivement 1 et 2 atomes d'oxygène en 45 minutes et 2 heures. En présence de faibles quantités d'acide perchlorique, l'oxydation est ralentie et les différences sont encore plus accentuées (Tableau I).

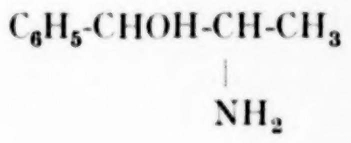
L'oxydation de la *pseudo*-noréphédrine (*thréo*) est également plus rapide que celle de son isomère *érythro*, la noréphédrine. La consommation limite d'oxygène correspond, après 3 heures, à un atome par molécule d'amino-alcool. Les différences d'oxydabilité entre les diastéréoisomères sont encore notables si les bases sont salifiées par un acide fort, tel que l'acide perchlorique. Avec les acétates, par contre, les différences sont beaucoup moins importantes.

L'oxydation des formes *thréo* et *érythro* du 1-phényl 2-amino propane 1,3-diol et du 1-*p*-nitrophényl 2-amino propane 1,3-diol répond au schéma (b). L'étude cinétique de l'oxydation montre encore une oxydation plus rapide des formes *thréo*.



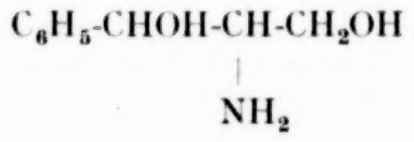
$CH_3\text{-}CHOH\text{-}\underset{NH_2}{CH}\text{-}COOH$

Thréonine



$C_6H_5\text{-}CHOH\text{-}\underset{NH_2}{CH}\text{-}CH_3$

Noréphédrine



$C_6H_5\text{-}CHOH\text{-}\underset{NH_2}{CH}\text{-}CH_2OH$

1-Phényl 2-amino propane
1,3-diol

Dans le cas des dérivés N-substitués des α,β-amino-alcools, les vitesses d'oxydation des diastéréoisomères sont sensiblement égales, aux erreurs expérimentales près.

Ce phénomène a été observé sur les couples:

- *pseudo*-éphédrine (*thréo*) et éphédrine (*érythro*)
- N-benzyl *pseudo*-noréphédrine (*thréo*) et N-benzyl noréphédrine (*érythro*).

Il peut être interprété par l'intervention de nouvelles conformations dans lesquelles l'un des groupes volumineux extrême est l'azote substitué, III et IV. Les diastéréoisomères *thréo* et *érythro* n'offrent alors plus de différence dans les distances azote–oxygène.

PARTIE EXPÉRIMENTALE

(avec Mlle G. CLEMENT)

Réactif

Le réactif est une solution 0.05*M* obtenue en dissolvant 2.22 g de tétracétate de plomb[15] dans 100 ml de mélange à parties égales de chloroforme et d'acide acétique.

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Oxydation quantitative

On pratique l'oxydation de la thréonine et de l'*allo*-thréonine sur des solutions 0.5M dans l'eau ou l'acide perchlorique 0.5N. L'éphédrine, la *pseudo*-éphédrine, la noréphédrine et la *pseudo*-noréphédrine ont été oxydées en solution M dans l'acide perchlorique N. Pour les isomères de la base du chloramphénicol et leurs analogues non nitrés, les solutions sont 0.5M dans l'acide perchlorique 0.5N.

A 20 ml de réactif tétracétique on ajoute 0.5 ml de solution d'amino-alcool et on maintient à 20°. Après un temps variable, on prélève 1 ml du mélange et dilue à 100 ml avec le mélange à parties égales chloroforme–acide acétique. La lecture est effectuée à 3,000Å sur spectrophotomètre Beckman DU.

RÉSUMÉ

L'étude de la scission des α,β-amino-alcools diastéréoisomères par le tétracétate de plomb permet de différencier les séries *thréo* et *érythro*. Un dosage spectrophotométrique du sel de plomb tétravalent montre que la thréonine, la *pseudo*-noréphédrine, le 1-*p*-nitrophényl 2-amino propane 1,3-diol *thréo* (base du chloramphénicol) et son analogue non nitré sont en effet oxydés plus rapidement que leurs isomères *érythro*. Les différences de vitesses d'oxydation s'annulent lorsqu'il y a substitution sur l'azote.

SUMMARY

A study of the splitting of the diastereoisomers of α,β-aminoalcohols with lead tetraacetate makes it possible to differentiate between the *threo*- and *erythro*-forms. Spectrophotometric analyses of the lead(IV) salts have shown that threonine, *pseudo*-norephedrine, *threo*-1-*p*-nitrophenyl-2-amino-propane-1,3-diol (ground substance of chloramphenicol) and its non-nitrated analogue are more rapidly oxidized than the isomers of the *erythro*-series. There is no difference in the rate of oxidation when substituents are attached to the nitrogen.

ZUSAMMENFASSUNG

Das Studium der Spaltung der Diastereoisomere der α,β-Amino-alkohole mit Bleitetraacetat ermöglicht die Unterscheidung zwischen den *threo*- und *erythro*-Formen. Eine spektrophotometrische Bestimmung des Blei(IV)-salzes zeigt, dass Threonin, *pseudo*-Norephedrin, *threo*-1-*p*-Nitrophenyl-2-amino-propan-1,3-diol (Grundkörper des Chloramphenicols) und dessen nichtnitriertes Analogon rascher oxydiert werden als die Isomeren der *erythro*-Reihe. Der Unterschied in der Oxydationsgeschwindigkeit verschwindet, wenn am Stickstoff Substitutionsgruppen sitzen.

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COULOMETRIC TITRATION WITH QUINQUEVALENT URANIUM

DETERMINATION OF VANADIUM(V)

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INTRODUCTION

Quinquevalent uranium was recently employed by Edwards and Kern[1] as a generated reagent for the reduction of ferric ion. The reducing power of the U(VI), U(V) couple ($E^\circ = +0.06$ V *vs.* S.H.E.) is surpassed only by that of Ti(III)[2] and Fe(II)EDTA[3] among coulometric reagents investigated to date. The danger of simultaneous hydrogen evolution prevents the generation of significantly stronger reducing agents at solid electrodes.

Uranium(V) is unstable with respect to disproportionation to U(VI) and U(IV); the rate is directly proportional to the hydrogen ion concentration[4]. The U(IV) produced in this reaction is neither as strong nor as rapid a reducing agent as U(V)[5]. Consequently the pH is preferably kept greater than 1 during coulometric titrations with this ion, in order that the disproportionation reaction should not compete with the titration reaction. This requirement is a disadvantage in the titration of such substances as hydrogen peroxide and dichromate ion, whose oxidizing power is much dependent on the acidity; in fact, U(V) cannot be used to titrate these two substances coulometrically. Vanadate, however, is reduced very well, no doubt because of the reversible nature[6] of the V(V), V(IV) couple ($E^\circ = +1.0$ V). The coulometric titration described in this paper provides a simple and reliable method for its determination. In particular, it permits the determination of vanadium in uranium samples without the addition of any reagent except what is required to adjust the pH within the limits 1–3. Iron and other rapid oxidizing agents are titrated along with the vanadium. This titration can be used to correct the coulometric uranium assay of Lingane and Iwamoto[2] for the presence of oxidizing impurities. These authors used Ti(III) as the generated reagent, which reduces iron and vanadium as well as uranium.

The problem of determining vanadium coulometrically in the presence of uranium was treated earlier by Furman, Reilley and Cooke[7]. These authors used ferrous ion as their reducing agent, generated from a ferric salt added to the uranium in large excess. Actually, the potentials are more favorable and the end-points sharper if the ferric ion is omitted, and the uranium employed as the source of reductant. Their method is useful for the selective determination of vanadium impurities. It can also be carried out in the presence of air, which must be carefully excluded when U(V) is the titrant because of its rapid air oxidation.

EXPERIMENTAL

Circuitry

The constant current source has been described previously[1]. A small drift in the

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line voltage was corrected by the use of a current stabilizer similar to that described by LINGANE[8]. This consisted of a Brown Electronik amplifier Type 358816 with associated 130-r.p.m. motor, which operated a 500-ohm Beckmann Type A Helipot resistor. The potential drop across a decade resistor in the constant current circuit was balanced against the E of a 1.5-V dry cell. Slight deviations in the generating current produced a net E which operated the motor and produced compensating changes in the Helipot resistor, which was likewise in the main current circuit. Total applied voltage in this circuit varied between 50 and 300 V. The current was held constant to within ± 0.02%.

For currents less than 0.1 mA, this entire apparatus could be replaced by a pair of 45-V B batteries, which gave currents that varied by less than 0.1% during the period required to carry out a titration.

Cells

Two cells were used, which are described fully elsewhere[1]. In the larger cell the cathode was a 20-cm^2 platinum sheet immersed in 0.03M UO_2Cl_2, the anode a platinum wire in 0.5M Na_2SO_4 solution. The two were separated by a glass frit and an agar plug.

For samples of less than 100 μg of vanadium, a smaller cell and cathode were employed. The anode consisted of a silver wire sealed in a tube completely filled with saturated KCl. The tube was suspended in the cathode compartment and made electrical contact with it through an upturned capillary of 0.5 mm diameter. This anode could not be used with currents exceeding 2 mA. Current fluctuations appeared which were ascribed to the small cross section of the wire and the capillary.

Reagents

We were fortunate in having a very pure sample of $VOSO_4 \cdot 3H_2O$ prepared by JONES AND COLVIN[9]. The salt had been dissolved in 0.6N H_2SO_4 and made up to 0.1000M in 1953. Titration with ceric sulfate and potassium permanganate in 1958 yielded concordant results, the average being 0.09987M. This result attests the stability of V(IV) solutions in stoppered soft glass bottles. Several aliquots were given a preliminary treatment with SO_2 before titration, to insure that all vanadium was present as V(IV). This treatment did not alter the titer. Vanadium(V) was therefore absent.

In addition, a second sample of $VOSO_4 \cdot 3H_2O$ was prepared in the manner of JONES AND COLVIN. The starting material was an impure $VOSO_4$ sample from A.D. Mackay Inc. The crystals were washed with acetone rather than alcohol, as the latter reagent gave an unmanageable sticky mass. This sample proved to have a slight excess of water, but was a satisfactory source of stock vanadium solution.

Uranyl chloride was prepared from Mallinckrodt uranyl nitrate by fuming with conc. HCl. The interference of nitrate in U(V) titrations has been discussed previously[1].

End-point determination

An amperometric method was used. About 0.25 V were applied across two small platinum gauze electrodes immersed in the catholyte. The electrodes were about 1 cm apart, and were placed outside the field between the generator electrodes. In the course of the titration the current rose and then fell to a sharp minimum at the end-point, followed by a steady increase thereafter. This type of indicator current curve is characteristic of reaction between two reversible couples[6].

Procedure

50-ml aliquots of stock vanadium(IV) solution were oxidized with Cl_2. The solution was boiled at length to remove excess oxidant. The volume of the solution was not permitted to shrink during this operation, since vanadium(V) readily precipitates as a basic salt on boiling, and redissolves only very slowly even if more H_2SO_4 is added to the solution. The resultant vanadium(V) solutions were diluted to strength and aliquots used for the titrations.

100 ml 0.03M UO_2Cl_2 served as the catholyte*. The acidity was adjusted to about pH = 1.5 by the dropwise addition of conc. HCl, and the solution then deaerated with nitrogen gas for 15 min. The vanadium solution was likewise deaerated with nitrogen that had been equilibrated by prior passage through a portion of the same solution.

Following a blank run with a few drops of vanadium solution, a series of 0.5-ml aliquots from a calibrated micropipet were analyzed in succession. During a run, U(V) was generated continuously until the indicator current showed that the end-point was near. The end-point was then reached by a series of small current increments. The first 0.1-sec excess of U(V) showed a clear and permanent increase in indicator current. Time was measured with an electric timer. Bubbling with nitrogen and magnetic stirring continued throughout the titrations.

RESULTS

The results for the titration of 0.014–2.5 mg samples are presented in Table I. The pH was in the range 1.5–1.9. The error curve was slightly displaced, the most probable error being +0.10%.

TABLE I

TITRATION OF VANADIUM(V) SAMPLES WITH GENERATED URANIUM(V)

mg Vanadium	*Current mA*	*Time sec*	*No. of trials*	*Limits of error, %*	*Average deviation from theoretical, %*
2.5	8–9	500–600	21	+0.47 —0.32	0.17
1.8	6–9	380–600	11	+0.39 +0.08	0.30
1.3	8	330	3	+0.1 —0.1	0.03
0.25	1	200–250	4	+0.20 —0.23	0.16
0.20	1	300–500	6	+0.43 +0.16	0.29
0.025	0.08–0.16	300–600	12	+0.33 —0.47	0.21
0.014	0.09	300	7	+0.90 —1.00	0.51

Effect of pH

The permissible upper limit is determined by the hydrolysis of uranyl ion, the lower by the disproportionation of U(V). Successful runs were made in the pH range 1.00–2.67. At pH = 3.28 no end-point was observed. The influence of more strongly acid solutions was not studied.

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* When the small cell was used, the volume of catholyte was 20 ml.

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Mixtures of Fe(III) and V(V)

Titrations of mixtures were carried out at pH 1.5. The results are given in Table II. The two ions were reduced together, yielding an indicator current curve similar to that of vanadium alone. Assuming the species making up the vanadium couple to be VO_2^{+2} and VO^{+2}, it is easily shown that the formal potential of the couple is about 0.82 V at pH 1.5, which does not differ materially from the 0.78 V value of the ferric-ferrous couple. The titration of ferric ion with U(V) is unsatisfactory[1] at acidities at which the couples might have sufficiently dissimilar potentials to yield two minima in the indicator current curve. Reduction of the indicator voltage to 0.01 did not change the shape of the curve.

TABLE II

TITRATION OF Fe(III)–V(V) MIXTURES

	Current *mA*	*Time* *sec*	*Error, %*
3 mg Fe + 5 mg V	15	1000	+0.6, +0.1, +0.3
3 mg Fe + 0.8 mg V	15	400	+0.2, −0.2, +0.4
3 mg Fe + 0.4 mg V	15	400	−0.1, +0.1

SUMMARY

Vanadium(V) has been determined by reduction with generated uranium(V) with an accuracy of about ± 0.3%. Amounts as small as 15 μg were successfully titrated. The suggested pH range is 1–2.5. Iron(III) is reduced simultaneously with vanadium(V).

RÉSUMÉ

Une méthode coulométrique est proposée pour le dosage du vanadium(V), à l'aide d'uranium(V).

ZUSAMMENFASSUNG

Es wird eine coulometrische Methode zur Bestimmung von Vanadium(V) mit Hilfe von Uranium(V) beschrieben.

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Received July 14th, 1958

REVUES DE LIVRE

Tratado de Quimica Analitica Cuantitativa, par Prof. Dr. F. BERMEJO MARTINEZ. Imprenta del Seminario Conciliar Santiago de Compostela, 1958, 1079 pages, 300 fig., 58 tables. Prix: 600 Ptas.

Le Professeur F. BERMEJO vient de publier un remarquable ouvrage de chimie analytique quantitative donnant une excellente vue d'ensemble de cette science et destiné tout spécialement à l'étudiant. En effet, ce dernier y trouvera d'utiles et précieux renseignements lui permettant d'acquérir les principes fondamentaux, les connaissances indispensables de l'analyse classique et les bases des techniques les plus récentes. Il y apprendra également comment apprécier les limites et déterminer les erreurs possibles des méthodes utilisées.

Voici, brièvement donné, un aperçu des différents chapitres traités, montrant l'importance de ce traité:

- classification des méthodes et opérations préliminaires,
- balance et pesée,
- analyse gravimétrique: théorie (produit de solubilité, effet de sel, coprécipitation électrolyse, électrolyse à potentiel contrôlé, etc.), appareillages et méthodes, description de dosages classiques,
- théorie des séparations (par précipitation, distillation, électrolyse, extraction, échange ionique, chromatographie),
- description de quelques séparations,
- analyse volumétrique: théorie (oxydo-réduction, acide-base, formation de complexes), appareillage et méthodes, dosages par oxydo-réduction (permanganométrie, dichromatométrie, cérimétrie, iodométrie, titanométrie, vanadométrie, etc.), dosages alcali-acidimétriques (également en milieu non aqueux), dosages par précipitation et formation de complexes,
- conductométrie et potentiométrie,
- polarographie, ampérométrie, coulométrie,
- spectrophotométrie par absorption (absorption dans le visible, l'ultra-violet, l'infra-rouge, les ondes ultra-courtes, spectres Raman, fluorométrie, néphélométrie, turbidimétrie, hétérométrie, etc.),
- spectrophotométrie par émission,
- application des rayons X et de la radioactivité à l'analyse,
- spectrométrie de masse,
- méthode de diffraction des électrons,
- microanalyse,
- calcul d'erreurs.

Signalons encore quelques tables (poids atomiques, logarithmes, concentrations, solutions tampons) et de nombreuses références bibliographiques.

C'est donc un ouvrage complet et moderne; bien que volumineux (1079 pages), il est bien ordonné, très clair et facile à consulter.

Le Professeur BERMEJO montre ainsi toute l'importance que prend à l'heure actuelle la chimie analytique, discipline indispensable à la formation du futur chimiste, qu'il se destine à l'analyse, à la recherche ou à l'industrie.

Nous félicitons l'auteur et nous sommes heureux de pouvoir recommander son traité.

Y. RUSCONI (Genève)

Spot Tests in Inorganic Analysis, par FRITZ FEIGL, traduit par RALPH E. OESPER, cinquième édition anglaise entièrement revue et augmentée, Elsevier Publishing Company, Amsterdam, 1958, 6×9, xiii +600 pp., £ 3.5.–.

Il y a quelque temps, nous avions le plaisir d'annoncer aux lecteurs des ,,*Analytica Chimica Acta*'' la cinquième édition du fameux ,,*Spot Tests in Organic Analysis*''.

Infatigable dans sa tâche et fidèle à son but, M. FEIGL nous présente aujourd'hui la première partie de cette oeuvre, le ,,*Spot Tests in Inorganic Analysis*'', en cinquième édition également.

Le livre, un classique dans son genre, est suffisamment connu des chimistes pour que nous n'insistions pas sur ses mérites. Nous ne saurions néanmoins passer sous silence les avantages qu'offre cette nouvelle édition vis-à-vis de la précédente. Ayant procédé à une revision complète de son oeuvre, M. FEIGL l'a enrichie de nombreuses nouvelles réactions et techniques améliorées, résultant pour la plupart de ses recherches personnelles. Le nombre des pages est ainsi porté à 600 contre les 451 de l'édition précédente. La disposition des chapitres est la même: Introduction, techniques à la touche (par M. P. W. WEST), réactions des cations, réactions des anions, réactions des éléments libres, analyse systématique des mélanges, applications pratiques, tableau résumant les réactions.

Nous tenons à recommander vivement ce livre à tous les chimistes, persuadés qu'il leur sera un guide des plus utiles, lorsqu'ils auront à effectuer un contrôle qualitatif quelconque.

I. KAPÉTANIDIS (Genève)

ANNOUNCEMENTS

XVe CONGRÈS INTERNATIONAL DE CHIMIE PURE ET APPLIQUÉE

Les nombreuses communications présentées au XVe Congrès International de Chimie Pure et Appliquée (Chimie Analytique) seront publiées en trois volumes.

Un premier volume, concernant les ,,Discours", les ,,Allocutions" et les ,,Communications" jusqu'à la fin de la 3ème Section est déjà imprimé. Les deux autres volumes, se rapportant aux autres sections, pourront être obtenus dans un court délai.

Ce volume I peut être commandé à l'adresse suivante:

Secretario-Geral do XV Congresso Internacional de Quimica Pura e Aplicada,
Instituto Superior Tecnico, Avenida Rovisco Pais, Lisboa, Portugal,

Le prix des trois volumes est de 320 escudos (par poste ordinaire, y inclus emballage et poste); par avion, le prix est de 330 escudos.

Le paiement pourra être effectué par n'importe quelle banque de Lisbonne.

LUIS ACCIAIUOLI
Secrétaire Général du Congrès

SYMPOSIUM ON INHALED PARTICLES AND VAPOURS

organized by

THE BRITISH OCCUPATIONAL HYGIENE SOCIETY

President: W. G. MARLEY,
Atomic Energy Research Establishment,
Harwell, Nr. Didcot, Berks.

Hon. Secretary: PETER C. G. ISAAC,
Public Health Engineering Laboratory,
King's College, Newcastle upon Tyne.

An International Symposium on Inhaled Particles and Vapours, organized by the British Occupational Hygiene Society, will be held in Oxford in April 1960. The Symposium will be concerned with the physical, chemical and physiological factors governing the entry of harmful substances into the body via the respiratory system.

The subjects of the Symposium have a bearing on many hygiene problems including silicosis, asbestosis and the other pneumoconioses, and on the damage to health produced by smog, tobacco smoke, radioactive gases and dusts, airborne bacteria and toxic vapours. The Society believes that the Symposium will meet a real need in providing an opportunity for the comprehensive discussion of recent research in this field and that the published proceedings will be of value not only to research workers, but also to those concerned with the practical problems of establishing and maintaining safe environments.

Contributions to the Symposium will be welcomed from all countries. The main language of the Symposium will be English and it is intended to circulate the papers in advance in this language, but it is hoped to be able to provide interpretation for those oral contributions to the discussion which may have to be made in French or German. Papers submitted will be subject to scrutiny by the Society's Honorary Editor, Dr. C. N. Davies, assisted by a panel of referees.

Those wishing to contribute are requested to notify the Chairman of the Organizing Committee, Mr. W. H. Walton, Assistant Director, Mining Research Establishment, National Coal Board, Worton Hall, Worton Road, Isleworth, Middlesex, as soon as possible, indicating the subject of their papers.

CHELATING PROPERTIES OF N,N,N',N'-TETRAKIS-(PHOSPHONOMETHYL)-1,2-CYCLOHEXANEDIAMINE*

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INTRODUCTION

Since the announcement about eleven years ago by SCHWARZENBACH and his co-workers[1] of a new volumetric method for determining the hardness of water by titration with ethylenediaminetetraacetic acid (EDTA or ENTA), the applications of chelate chemistry to analytical problems have been exceedingly numerous. The versatility of chelating agents as analytical reagents has resulted in considerable research in connection with the synthesis of new and different compounds. Many of the substances investigated contain carboxy groups and coordinate with the metal ion through oxygen atoms. It was considered to be of interest to investigate the possibility of a chelating agent containing some group other than the carboxy group which would still permit oxygen-to-metal bonds.

For many years various arsonic acids have been developed and used analytically[2]. The periodic relations between arsenic and phosphorus lead one to believe that phosphonic acids should be investigated for their analytical applications.

This work was a study of the preparation of a phosphonic acid chelating agent, N,N,N',N'-tetrakis-(phosphonomethyl)-1,2-cyclohexanediamine, and of some of its properties. A trivial name for the compound is cyclohexanediaminetetramethylphosphonic acid, or simply abbreviated to CDTMP.

PREPARATION

One of the general methods for the preparation of EDTA and related compounds involves the condensation of an amine with a halo acid, generally a chloro acid, in alkaline solution[3-5]. This procedure is quite versatile and nearly any kind of acid group can be attached to almost any amine. BERSWORTH[6] used this method to prepare N,N,N',N'-tetrakis-(phosphonomethyl)-ethylenediamine.

In this work, chloromethylphosphonic acid was reacted with 1,2-cyclohexanediamine in alkaline solution to prepare the desired compound.

Chloromethylphosphonic acid

Chloromethylphosphonic acid was prepared by causing phosphorus(III) chloride to react with paraformaldehyde[7]. A two-step reaction was used, according to the following procedure.

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* Abstracted from a dissertation submitted by ROGER E. YERICK to the Graduate Faculty of Iowa State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1957.

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*** Contribution No. 648. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

20 g of paraformaldehyde were placed in a 500-ml two-necked reaction flask, fitted with standard taper joints. A reflux condenser and an addition funnel were put in place. A magnetic stirrer was used to provide the necessary agitation. 90 ml (142 g) of phosphorus(III) chloride were placed in the addition funnel. About 15 ml of this were added rapidly to the paraformaldehyde. After a few minutes a rather vigorous reaction occurred, during which considerable heat was evolved and most of the paraformaldehyde went into solution. When this reaction had subsided completely, stirring was begun and the remainder of the phosphorus(III) chloride was added at the rate of about 5 ml/min. When the addition was complete, the mixture was allowed to stir for an additional 10 min.

The mixture was sealed in a glass tube of about 400-ml capacity that had been constructed from medium-wall borosilicate glass tubing. The sealed tube was placed inside a piece of steel pipe that had been threaded at each end and fitted with pipe caps. This assembly was put into an oven which had been brought to a temperature of 240°–250°. During the first 2 h of heating, the pipe was removed from the oven at 30-min intervals and shaken briefly in order to thoroughly mix the contents of the sealed tube. The total heating period was 12 h.

At the end of the heating period, the sealed tube was allowed to cool to room temperature and its contents removed. At this stage, the product was dark brown or black in color. The crude product was fractionated and the portion of the distillate boiling between 93° and 98° at 17 mm of Hg pressure was collected. This fraction was chloromethylphosphonic dichloride.

Hydrolysis of the dichloride to yield the acid was accomplished by slowly adding the dichloride to a 50% excess of water with constant stirring. The water was removed by vacuum evaporation, never allowing the temperature of the mixture to exceed 30°. The resulting chloromethylphosphonic acid was a hygroscopic solid that crystallized in the form of long needles. It was stored in a vacuum desiccator containing phosphorus(V) oxide. The product, as isolated at this point, was satisfactory for the synthesis of CDTMP. It was possible to further purify it, if desired, by redissolving in water, treating with charcoal until a water-white filtrate was obtained and again removing the excess water by vacuum evaporation.

N,N,N′,N′-tetrakis-(phosphonomethyl)-1,2-cyclohexanediamine

CDTMP was prepared by reacting chloromethylphosphonic acid with 1,2-cyclohexanediamine in an alkaline solution. The diamine used was obtained in the form of the sulfate salt from Geigy Industrial Chemicals, New York, N.Y. The procedure developed was the following.

An amount of the diamine weighing 106 g was dissolved in approximately 500 ml of 15% (w/v) aqueous sodium hydroxide. This was extracted with 600 ml of ethyl ether in four portions of 200 ml, 200 ml, 100 ml, and 100 ml. The ether was removed by distillation to leave the free diamine, which was a pale yellow, oily liquid. Approximately 275 g of chloromethylphosphonic acid (the mole ratio of acid to diamine should be slightly more than 4:1) were dissolved in 600 ml of water. Sodium hydroxide pellets were added slowly and with constant stirring until a pH of 10–11 was obtained. Then the solution was saturated with sodium carbonate.

The free diamine was placed in a three-necked reaction flask of 3 l capacity which had been fitted with a reflux condenser and 75 ml of water were added. The pH was adjusted to 10–11 with sodium hydroxide and the solution heated to boiling. The chloromethylphosphonic acid solution was added at the rate of about 20 ml/min by means of an addition funnel. When all the acid had been added, the heat was adjusted to give moderate refluxing and the reaction was allowed to proceed for about 90 h.

At the end of the reflux period, the reaction mixture was allowed to cool and concentrated hydrochloric acid was added until the pH was lowered to about 6.5; the solution was filtered and the filtrate evaporated on a steam bath until a thick syrup was obtained. Approximately 250 ml of water were added and the mixture was heated and stirred for 10 min. It was filtered to remove any solids present and the residue was discarded.

To the filtrate was added an equal volume of ethyl alcohol. Two liquid phases resulted, the lower one containing the desired product. The mixture was stirred and the upper phase decanted. Another volume of alcohol was added and this procedure repeated. Successive portions of alcohol were added, followed by stirring and decantation until the lower phase had become jelly-like in character. Then another volume of alcohol was added and the mixture was stirred until it had the consistency of putty.

This solid was dissolved in as little water as possible without heating and was treated with decolorizing charcoal until a water-white filtrate was obtained. The alcohol-precipitation procedure was repeated, and the product was tested for the presence of chloride. If this test proved to be positive, the dissolution-precipitation procedure was repeated a third time. Generally, this served to remove all the chloride and presumably the other inorganic materials that were present in the original reaction mixture.

The product, as obtained at this stage, was a mixture of various partially-neutralized forms of CDTMP. In order to obtain completely the octasodium salt, the product was once again dissolved in a minimum amount of water and about 1 g of sodium hydroxide was added for every 10 g of product. After precipitation again by means of ethyl alcohol, the material was washed with about 1 l of the absolute ethyl alcohol and transferred to a crystallizing dish and placed in a vacuum desiccator containing phosphorus(V) oxide. The material was a white, rather hygroscopic solid; the yield was approximately 45%.

The octasodium salt was analyzed for sodium and phosphorus. Sodium: theoretical = 27.62%, found = 27.72%; phosphorus: theoretical = 18.59%, found = 18.66%.

IONIZATION CONSTANTS OF CDTMP

Aqueous titrations of the octasodium salt of CDTMP with acid resulted in a titration curve with two breaks. The first of these occurred at two moles of acid added per mole of salt initially present and the second at six moles of acid per mole of salt. A sample titration curve is given in Fig. 1. Although the titrations were done using samples of the octasodium salt, the explanation is perhaps more straightforward when approached from the standpoint of the free acid. However, it was impossible to isolate this in a form other than a thick syrup. The information obtained, though, lends itself to the following interpretation.

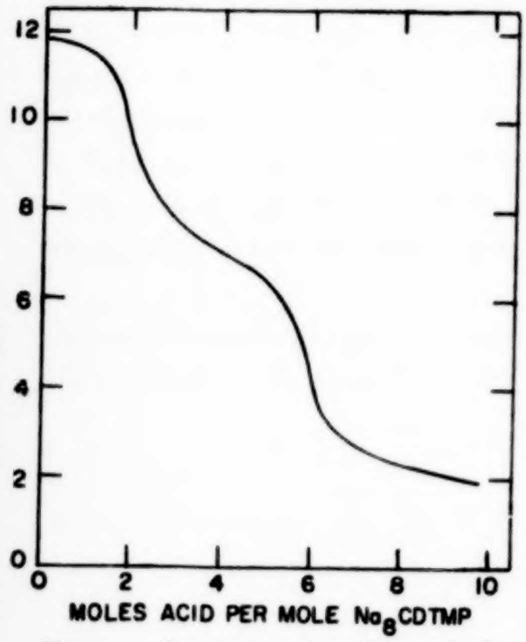

Fig. 1. Aqueous titration of the octasodium salt of CDTMP.

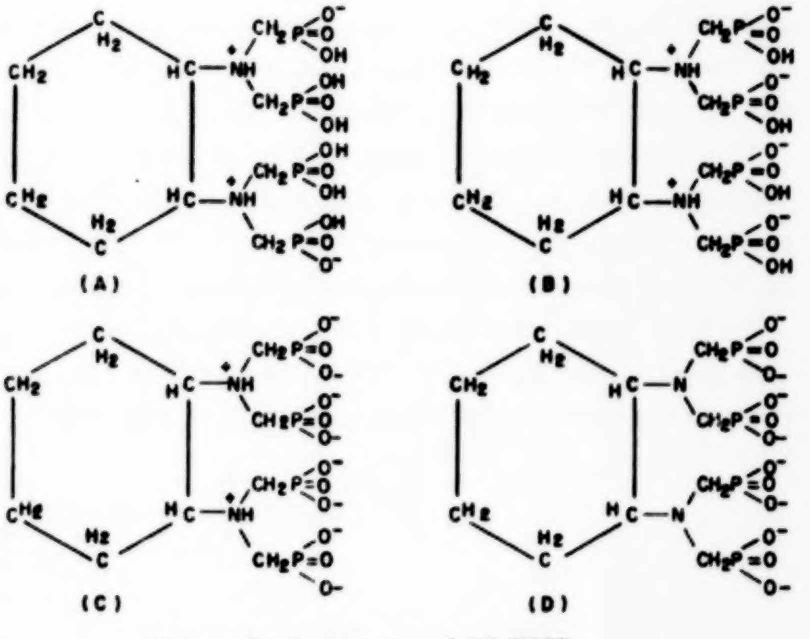

Fig. 2. Ionic species of CDTMP.

A double-dipolar structure, as indicated by (A) of Fig. 2 represents the free acid in solution. The first break in the titration curve represents the consumption of two moles of base per mole of acid, and the species present at this point is indicated by (B) of Fig. 2. Here, the two most acidic protons have been removed. These were originally on the phosphonic acid groups that contained two protons each, as shown in (A). This gives rise to a weak buffer region, and the removal of the protons remaining on the phosphonic acid groups is represented by only one break since they are about of the same acid strength. Hence, the species present at the second break in the titration curve is shown in (C) of Fig. 2. The two protons attached to the nitrogens are too weakly acidic in character to give a break in the titration curve, and the completely neutralized compound is represented by (D) of Fig. 2.

The method used for the determination of the eight ionization constants of the acid form of CDTMP was an extension of a procedure first suggested by SCHWARZENBACH, WILLI AND BACH[8]. In this study it was necessary to determine eight ionization constants from a titration curve possessing only two breaks.

The mathematical treatment connected with the determination of the ionization constants required that each point on the aqueous titration curve be expressed as a function of the total concentration of CDTMP in the solution, C_s, the hydrogen-ion concentration, the moles of base added per mole of CDTMP, the eight ionization constants of CDTMP, and the various ionic species of CDTMP present in the solution. However, it was possible to make use of certain simplifications in specific areas of the titration curve. An examination of the titration curve for CDTMP showed that the first break occurred at $b = 2$ and the second break at $b = 6$, where b represents the number of moles of base added per mole of CDTMP initially present. This meant that the several ionization constants could be grouped in the following ways for purposes of calculation. Only the first two ionization constants, K_1 and K_2, were considered up to the first break. In the region between the two breaks, only K_3, K_4, K_5, and K_6 were taken into account. After the second break, all except K_7 and K_8 were neglected.

For purposes of calculation, the various ionic species were represented as $[H_8R]$, $[H_7R^-]$, $[H_6R^{-2}]$, $[H_5R^{-3}]$, $[H_4R^{-4}]$, $[H_3R^{-5}]$, $[H_2R^{-6}]$, $[HR^{-7}]$, and $[R^{-8}]$. For purposes of simplification, later references to these species will omit the usual indication of the sign and magnitude of the charge on the ions.

In the region of the titration curve between $b = 0$ and $b = 2$, the data obtained was used to calculate the values of the first two ionization constants, K_1 and K_2. The expression derived for their calculation was this:

$$g + (g-1)\frac{K_1}{[H]} + (g-2)\frac{K_1K_2}{[H]^2} = 0 \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$\text{where } g = \left(b + \frac{[H]}{C_s} - \frac{[OH]}{C_s}\right).$$

The only unknown terms were the two ionization constants; hence, two sets of values of C_s, b, and pH permitted the solution of two simultaneous equations for the individual values of K_1 and K_2.

Data taken from the region of the titration curve between the two breaks (*i.e.*, between $b = 2$ and $b = 6$) were used to determine the numerical values of K_3, K_4, K_5, and K_6. The final equation derived was as follows:

$$(g-2) + (g-3)\frac{K_3}{[H]} + (g-4)\frac{K_3K_4}{[H]^2} + (g-5)\frac{K_3K_4K_5}{[H]^3} + (g-6)\frac{K_3K_4K_5K_6}{[H]^4} = 0 \quad (2)$$

$$\text{where } g = \left(b + \frac{[H]}{C_s} - \frac{[OH]}{C_s}\right).$$

Four sets of values of C_s, b, and pH were required to give the necessary number of simultaneous equations.

Values of K_7 and K_8 were obtained from data derived from that part of the titration curve bounded by $b = 6$ and $b = 8$. The expression used was this:

$$(g—6) + (g—7)\frac{K_7}{[\mathrm{H}]} + (g—8)\frac{K_7K_8}{[\mathrm{H}]^2} = 0 \quad \ldots\ldots\ldots\ldots \quad (3)$$

$$\text{and again, } g = \left(b + \frac{[\mathrm{H}]}{C_s} - \frac{[\mathrm{OH}]}{C_s}\right).$$

Two solutions of the octasodium salt of CDTMP were prepared and sufficient perchloric acid was added to each to effectively give the acid form of the compound. The ionic strength was maintained at 0.1 by the use of sodium perchlorate and the temperature was kept at 25°. The solutions were titrated with sodium hydroxide. A Beckman, Model G, pH meter equipped with a calomel and Type E glass electrode was used to measure the pH. The concentrations of the solutions were determined by inspection of the titration curves. Knowing the normality of the sodium hydroxide and the volume of base required between the two breaks (which represented the titration of four protons), the amount of CDTMP present was calculated. Also from this, the amount of sodium hydroxide required to titrate the excess perchloric acid present was determined. In all the calculations, the decrease in C_s caused by the increase in total volume during the course of the titration was considered.

The results of the titrations and calculations are expressed in Tables I, II, and III.

It was of interest to determine just how well the experimentally obtained values of the ionization constants fitted with the potentiometric titration curve. Therefore, using the experimental values of $K_1 \ldots K_8$ in conjunction with eqns. (1), (2), and (3), various values of b were calculated for given values of pH. Table IV gives the results of these calculations, and a graphic comparison is shown in Fig. 3.

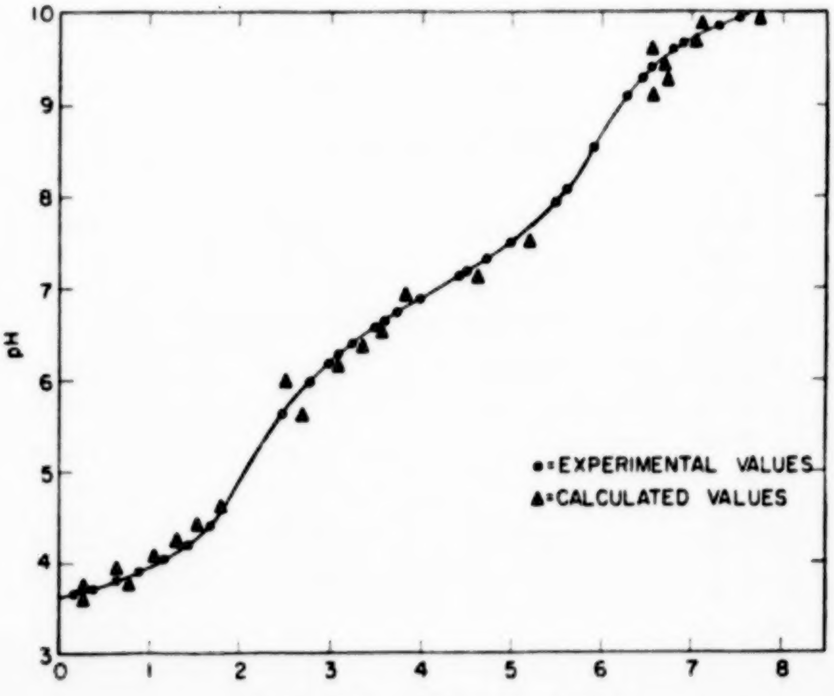

Fig. 3. Titration of CDTMP with sodium hydroxide.

TABLE I

APPARENT IONIZATION CONSTANTS OF CDTMP
CALCULATION OF K_1 AND K_2

b	*pH*	$K_1 \cdot 10^3$	$K_2 \cdot 10^4$
		CDTMP Solution I	
0.120	3.66	3.52	1.46
0.899	3.90		
0.380	3.72	3.91	1.92
1.160	4.02		
1.420	4.19	4.63	2.76
1.835	4.60		
0.639	3.81	4.29	2.58
1.679	4.41		
		CDTMP Solution II	
0.213	3.76	3.91	1.95
1.019	4.08		
0.747	3.96	4.78	2.91
1.509	4.45		
1.291	4.26	3.61	1.58
1.726	4.47		
1.400	4.35	3.84	1.63
1.888	5.02		

Average $K_1 = 4.07 \cdot 10^{-3}$; p$K_1 = 2.40$
Average $K_2 = 2.10 \cdot 10^{-4}$; p$K_2 = 3.70$

TABLE II

APPARENT IONIZATION CONSTANTS OF CDTMP. CALCULATION OF K_3, K_4, K_5 AND K_6

b	*pH*	$K_3 \cdot 10^6$	$K_4 \cdot 10^7$	$K_5 \cdot 10^7$	$K_6 \cdot 10^8$
		CDTMP Solution I			
2.460	5.65	4.37	3.16	0.82	1.65
2.964	6.20				
3.469	6.60				
3.974	6.90				
2.763	6.00	4.56	3.28	0.94	1.81
3.217	6.41				
4.426	7.03				
4.983	7.50				
3.066	6.29	4.79	3.61	1.28	2.27
3.571	6.67				
4.478	7.18				
5.493	7.96				
3.721	6.74	4.91	3.88	1.52	2.50
4.731	7.32				
5.595	8.07				
5.901	8.55				

(Contd. on p. 307)

TABLE II (Continued)

b	pH	$K_3 \cdot 10^6$	$K_4 \cdot 10^7$	$K_5 \cdot 10^7$	$K_6 \cdot 10^8$
CDTMP Solution II					
2.216	5.56	4.86	3.52	1.28	2.07
2.761	6.17				
3.086	6.42				
3.625	6.77				
2.432	5.83	5.19	4.19	1.73	2.83
2.870	6.27				
3.305	6.58				
3.995	6.97				
2.542	5.96	4.23	3.02	0.65	1.70
3.195	6.52				
4.259	7.10				
4.894	7.45				
3.467	6.68	4.57	3.31	0.96	1.91
4.417	7.18				
5.209	7.67				
5.580	7.99				

Average $K_3 = 4.68 \cdot 10^{-6}$; p$K_3 = 5.32$
Average $K_4 = 3.47 \cdot 10^{-7}$; p$K_4 = 6.46$
Average $K_5 = 1.15 \cdot 10^{-7}$; p$K_5 = 6.97$
Average $K_6 = 2.09 \cdot 10^{-8}$; p$K_6 = 7.69$

TABLE III

APPARENT IONIZATION CONSTANTS OF CDTMP
CALCULATION OF K_7 AND K_8

b	pH	$K_7 \cdot 10^{10}$	$K_8 \cdot 10^{11}$
CDTMP Solution I			
6.258	9.10	3.98	1.38
6.767	9.60		
6.565	9.42	3.72	1.09
7.532	9.99		
6.869	9.67	3.53	0.71
7.787	10.06		
6.461	9.33	4.57	1.93
7.277	9.89		
CDTMP Solution II			
6.454	9.33	4.79	2.17
7.095	9.80		
6.668	9.52	4.01	1.65
7.735	10.07		
6.134	8.80	3.62	0.91
6.508	9.38		
6.775	9.60	3.89	1.02
7.468	9.98		

Average $K_7 = 4.02 \cdot 10^{-10}$; p$K_7 = 9.39$
Average $K_8 = 1.36 \cdot 10^{-11}$; p$K_8 = 10.89$

Attempts were made to fit the experimental curve in Fig. 3 by using only three constants, *i.e.*, $K_1' = (K_1K_2)^{\frac{1}{2}}$, $K_2' = (K_3K_4K_5K_6)^{\frac{1}{4}}$, and $K_3' = (K_7K_8)^{\frac{1}{2}}$. However, in this case, the agreement between the calculated and experimental curves was very poor.

STABILITIES OF CDTMP CHELATES

Potentiometric methods

Qualitative studies indicated that CDTMP reacted with numerous metal ions in a manner not unlike the common chelating agents. However, it was also found that most of the complexes formed were too weak to be of significant analytical use.

The nature of the complexes was investigated by the method of continuous variations[9,10]. Not all the chelates were subjected to this study, because it was felt that those studied were representative. In all cases it was found that a 1 : 1 chelate between the metal ion and CDTMP was formed.

TABLE IV

COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF *b*

b, *exptl.*	*pH*	*b*, *calc.*	*b*, *exptl.*	*pH*	*b*, *calc.*
0.120	3.66	0.260	3.721	6.74	3.863[a]
0.380	3.72	0.213	3.974	6.90	3.782
0.639	3.81	0.771	4.426	7.03	4.638
0.899	3.90	0.640	4.478	7.18	4.263[a]
1.160	4.02	1.072	4.731	7.32	4.488[a]
1.420	4.19	1.331	5.493	7.96	5.714[a]
1.679	4.41	1.515	5.595	8.07	5.266[a]
1.835	4.60	1.792	5.901	8.55	6.399[a]
2.460	5.65	2.674	6.258	9.10	6.537
2.763	6.00	2.501	6.461	9.33	6.737
2.964	6.20	3.079	6.565	9.42	6.681
3.066	6.29	2.802[a]	6.767	9.60	6.502
3.217	6.41	3.329	6.869	9.67	6.993
3.469	6.60	3.560	7.277	9.89	7.105
3.571	6.67	3.702[a]	7.532	9.99	7.722
			7.787	10.06	7.519

[a] Not plotted in Fig. 3.

The stabilities of most of the metal chelates were measured by a potentiometric procedure resulting from an extension of a method used by CARINI AND MARTELL[11]. The stability constants of the cobalt(II), nickel(II), and iron(III) chelates were determined by spectrophotometric methods.

The potentiometric determination of the chelate stabilities involved the titration of CDTMP in the presence of about a 20-fold excess of the metal ion being studied. The ionic strength was adjusted to 0.1 with sodium perchlorate and the temperature was maintained at 25°. From a knowledge of the equilibria involved, it was possible to derive an expression in which the only unknown was K_m, which represented the stability constant of the metal–CDTMP complex under investigation. The final form of the equation developed was this:

$$K_m [M] (4C_s - E) = E\left(\frac{[\mathrm{H}]^8}{L_1} + \frac{[\mathrm{H}]^7}{L_2} + \frac{[\mathrm{H}]^6}{L_3} + \frac{[\mathrm{H}]^5}{L_4} + \frac{[\mathrm{H}]^4}{L_5} + \frac{[\mathrm{H}]^3}{L_6} + \frac{[\mathrm{H}]^2}{L_7} + \frac{[\mathrm{H}]}{K_8} + 1\right) + C_s\left(\frac{4[\mathrm{H}]^8}{L_1} + \frac{3[\mathrm{H}]^7}{L_2} + \frac{2[\mathrm{H}]^6}{L_3} + \frac{[\mathrm{H}]^5}{L_4} - \frac{[\mathrm{H}]^3}{L_6} - \frac{2[\mathrm{H}]^2}{L_7} - \frac{3[\mathrm{H}]}{K_8} - 4\right) \quad \ldots\ldots \quad (4)$$

where $E = (b-4)C_s + [\mathrm{H}] - [\mathrm{OH}]$,
b = moles sodium hydroxide per mole of CDTMP present,
C_s = total concentration of CDTMP present,
$L_1 = K_1K_2K_3K_4K_5K_6K_7K_8$,
$L_2 = K_2K_3K_4K_5K_6K_7K_8$,
$L_3 = K_3K_4K_5K_6K_7K_8$,
$L_4 = K_4K_5K_6K_7K_8$,
$L_5 = K_5K_6K_7K_8$,
$L_6 = K_6K_7K_8$,
$L_7 = K_7K_8$, and
the K's are the individual ionization constants of CDTMP.

The results of the titrations are presented in Figs. 4 and 5. The calculated values of the stability constant for the CDTMP–magnesium complex are given in Table V. A summary of the stability constants determined by the potentiometric method are given in Table VI.

Spectrophotometric methods

The stability constants of CDTMP chelates with cobalt(II) and nickel(II) could not be determined by the potentiometric method because of hydrolysis of the metal ions during the course of the titration. Instead, a spectrophotometric procedure was employed. In this study the pH was adjusted to approximately 11. Thus, all of the CDTMP was considered to be in the completely ionized form, and the only species considered was $[\mathrm{R}^{-8}]$. This aided in the calculations, and as long as an excess of CDTMP

TABLE V

STABILITY OF CDTMP–MAGNESIUM COMPLEX

b	pH	$K_m \cdot 10^{-6}$	b	pH	$K_m \cdot 10^{-6}$
6.084	6.59	1.01	7.054	6.78	2.10
6.192	6.60	1.14	7.162	6.82	2.88
6.300	6.62	1.79	7.269	6.85	3.18
6.408	6.64	1.32	7.377	6.89	2.83
6.515	6.67	2.08	7.485	6.95	2.96
6.622	6.69	2.41	7.593	7.03	1.27
6.731	6.72	1.92	7.700	7.14	3.71
6.838	6.74	3.26	7.862	7.34	4.51
6.946	6.76	2.69	7.970	7.57	4.83

Average $K_m = 2.55 \pm 0.87 \cdot 10^6$, $t = 25°$, $\mu = 0.1$.

was present in the solution, no hydrolysis of the metal ion was encountered. The basic working equation derived was this:

$$A_t = (\varepsilon_2)\,(a)\,[\mathrm{R}] + \frac{(\mathrm{M}_t)\,(a)\,(\varepsilon_2) + (\mathrm{M}_t)\,(a)\,(\varepsilon_3)\,(K_m)\,[\mathrm{R}]}{1 + K_m[\mathrm{R}]} \qquad (5)$$

where A_t = total measured absorbance,
a = cell length,
ε_1 = molar absorptivity of M, the metal,
ε_2 = molar absorptivity of R, the reagent,
ε_3 = molar absorptivity of MR, the chelate,
K_m = stability constant of the chelate, and
M_t = total metal concentration.

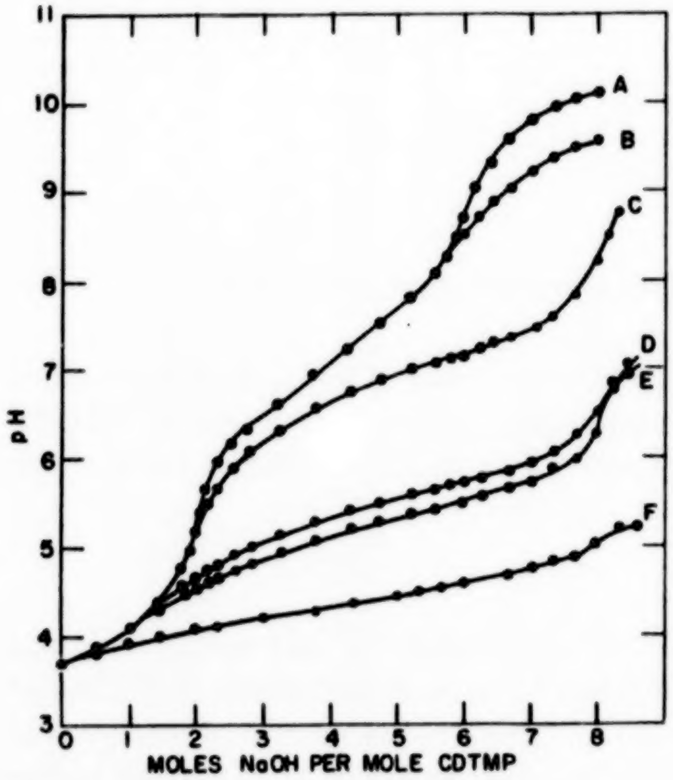

Fig. 4. Titration curves of CDTMP: curve A, CDTMP; curve B, CDTMP + barium; curve C, CDTMP + calcium; curve D, CDTMP + manganese(II); curve E, CDTMP + cadmium; curve F, CDTMP + copper(II).

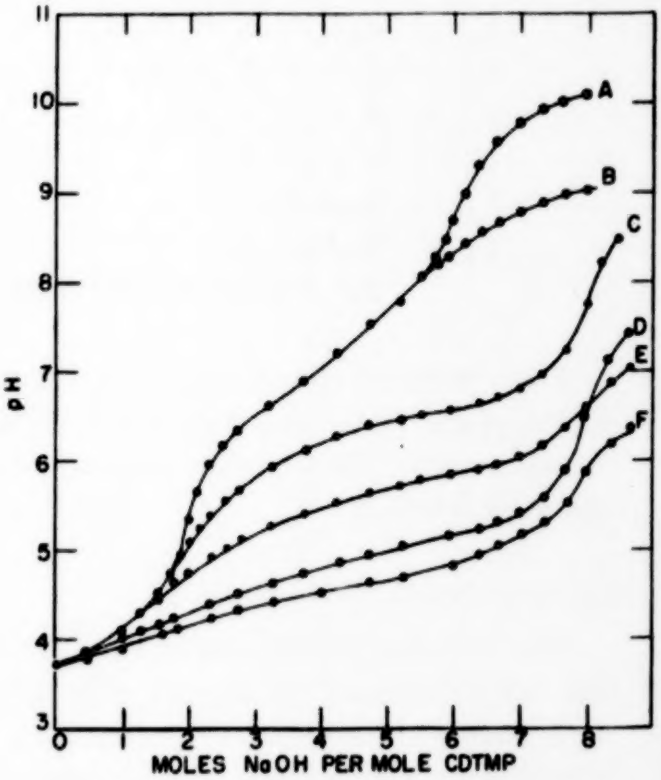

Fig. 5. Titration curves of CDTMP: curve A, CDTMP; curve B, CDTMP + strontium; curve C, CDTMP + magnesium; curve D, CDTMP + zinc; curve E, CDTMP + lead; curve F, CDTMP + mercury(II).

Under the conditions chosen for this study, there was no appreciable absorbance due to CDTMP itself; hence, the ε_2 term was neglected. The value of ε_1 was determined from measurements made on a solution containing only the metal ion in question. By the use of a series of successive approximations, it was possible to replace [R] by R_t, the total amount of R originally added. Thus, the only unknowns were the values of K_m and ε_3, and the solution of two simultaneous equations was necessary. The data taken and the results of the calculations for chelates of cobalt(II) and nickel(II) are presented in Tables VII and VIII.

The stability constant of the iron(III)–CDTMP chelate was determined spectrophotometrically by consideration of equilibria in acid solution. If an aqueous solution of CDTMP is adjusted to a pH of about 1.5, then for all practical purposes all of the

TABLE VI

STABILITY OF CDTMP–METAL COMPLEXES[a]

Metal	*Average K_m*
Magnesium	$2.55 \pm 0.87 \cdot 10^6$
Calcium	$3.12 \pm 0.91 \cdot 10^5$
Strontium	$5.27 \pm 1.09 \cdot 10^3$
Barium	$7.49 \pm 1.93 \cdot 10^2$
Zinc	$1.31 \pm 0.37 \cdot 10^9$
Cadmium	$1.15 \pm 0.35 \cdot 10^8$
Mercury(II)	$3.26 \pm 1.05 \cdot 10^9$
Lead	$9.75 \pm 2.14 \cdot 10^7$
Manganese(II)	$3.09 \pm 1.02 \cdot 10^8$
Copper(II)	$5.37 \pm 0.99 \cdot 10^9$

[a] $t = 25°$, $\mu = 0.1$.

CDTMP may be considered to be in the form of the acid, H_8R. This makes possible some simplifications in the equilibria involved.

In an acid solution, the reaction between iron(III) and CDTMP was expressed as follows:

$$Fe^{+3} + H_8R \rightleftharpoons FeH_{(8-n)}R^{-(n-3)} + nH^+ \quad \text{(a)}$$

It was necessary to devise some means of establishing the value of n and also of measuring the amount of iron(III) chelate present. This was done by first assuming the following reaction:

$$Fe^{+3} + H_8R \rightleftharpoons FeR^{-5} + 8H^+ \quad \text{(b)}$$

TABLE VII

STABILITY OF CDTMP–COBALT(II) COMPLEX

Solution No.	$M_t \cdot 10^3$	$R_t \cdot 10^3$	*pH*	A_t	ε_2	$K_m \cdot 10^{-3}$
1	1.86	3.72	11.08	0.497	64.2	1.27
2	1.86	4.65	11.13	0.501		
3	1.86	5.58	11.05	0.508	61.8	2.38
4	1.86	6.51	11.13	0.513		
5	1.86	7.44	11.21	0.520	58.2	4.35
6	1.86	8.37	11.07	0.524		
7	1.86	9.30	11.02	0.528	67.4	0.76
8	1.86	10.23	11.08	0.533		
9	1.86	11.16	11.23	0.548	65.5	0.97
10	1.86	12.09	11.16	0.554		
11	1.86	13.02	11.03	0.560	63.9	1.46
12	1.86	13.95	11.14	0.566		
13	1.86	14.88	11.09	0.569	59.8	3.18
14	1.86	15.81	11.17	0.573		

Average $K_m = 2.05 \pm 0.67 \cdot 10^3$, $t = 25°$, $\mu = 0.1$.

TABLE VIII

STABILITY OF CDTMP–NICKEL(II) COMPLEX

Solution No.	$M_t \cdot 10^3$	$R_t \cdot 10^3$	pH	A_t	ε_3	$K_m \cdot 10^{-3}$
1	1.86	3.72	11.22	0.636	79.8	7.47
2	1.86	4.65	11.28	0.640		
3	1.86	5.58	11.31	0.643	76.2	10.02
4	1.86	6.51	11.25	0.648		
5	1.86	7.44	11.06	0.654	79.1	7.19
6	1.86	8.37	11.13	0.657		
7	1.86	9.30	11.04	0.662	83.7	4.93
8	1.86	10.23	11.15	0.666		
9	1.86	11.16	11.22	0.669	72.3	12.18
10	1.86	12.09	11.07	0.671		
11	1.86	13.02	11.18	0.674	78.6	7.84
12	1.86	13.95	11.26	0.677		
13	1.86	14.88	11.01	0.679	73.5	11.76
14	1.86	15.81	11.14	0.681		

Average $K_m = 8.77 \pm 2.17 \cdot 10^3$, $t = 25°$, $\mu = 0.1$.

Insofar as spectrophotometric measurements were concerned, it was possible to derive this relationship (assuming a cell length of 1 cm):

$$A_t = \varepsilon_2 [\mathrm{H_8R}] + \frac{\mathrm{Fe}_t(\varepsilon_1[\mathrm{H}]^8 + \varepsilon_3 K_f[\mathrm{H_8R}])}{[\mathrm{H}]^8 + K_f[\mathrm{H_8R}]} \quad \ldots\ldots\ldots\ldots\ldots \quad (6)$$

where $K_f = \dfrac{[\mathrm{FeR}^{-5}][\mathrm{H}^+]^8}{[\mathrm{Fe}^{+3}]\,[\mathrm{H_8R}]}$,

A_t = total measured absorbance,
ε_1 = molar absorptivity of Fe, the metal,
ε_2 = molar absorptivity of H_8R, the reagent, and
ε_3 = molar absorptivity of FeR, the chelate.

The only unknowns were K_f and ε_3, because H_8R was established, as before, by successive approximations.

Using equation (6) as a starting point, it was possible to calculate a value for K_f by measuring the absorbances of a series of solutions at constant pH containing a varying iron(III) : CDTMP ratio. Also, it was possible to write an expression for the total absorbance in terms of the unknown power of [H] as indicated by reaction (a):

$$A_t = \varepsilon_2[\mathrm{H_8R}] + \frac{\mathrm{Fe}_t\varepsilon_1[\mathrm{H}]^n + \mathrm{Fe}_t\varepsilon_3 K_f[\mathrm{H_8R}]}{[\mathrm{H}]^n + K_f[\mathrm{H_8R}]} \quad \ldots\ldots\ldots\ldots\ldots \quad (7)$$

Data were obtained for eqn. (7) by measuring the absorbances of a series of solutions containing a constant iron(III) : CDTMP ratio but varying pH. Then assuming the first value obtained for K_f, the value of n was determined. This value of n was used to

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calculate a new value for K_f. Repeating this process until constant values for n and K_f were obtained gave the desired results.

As a result of the calculations, it was found that

$$n = 6.13 \pm 0.67 \text{ and}$$
$$K_f = 6.44 \pm 1.95 \cdot 10^{-10}.$$

Accordingly, the reaction between iron(III) and CDTMP in acid solution was assumed to be the following:

$$Fe^{+3} + H_8R \rightleftharpoons FeH_2R^{-3} + 6H^+ \quad \ldots\ldots\ldots\ldots \quad (c)$$

The value for K_f applies to the equilibrium described in reaction (c). A more usual form for expressing the formation of the complex is given by this reaction:

$$Fe^{+3} + H_2R^{-6} \rightleftharpoons FeH_2R^{-3} \quad \ldots\ldots\ldots\ldots\ldots \quad (d)$$

The equilibrium constant for this reaction was obtained by dividing K_f by the product $K_1K_2K_3K_4K_5K_6$, where $K_1 \ldots K_6$ were the values of the individual ionization constants for CDTMP as previously determined. When this was done, the value for K_m for the iron(III)–CDTMP chelate was given as:

$$K_m = \frac{6.44 \pm 1.95 \cdot 10^{-10}}{3.09 \cdot 10^{-33}} = 2.06 \pm 0.63 \cdot 10^{23}.$$

TABLE IX

TITRATION OF IRON(III) WITH CDTMP IN PRESENCE OF VARIOUS CATIONS

Metal added	*Ratio metal : Fe(III)*	*Fe(III) found*[a] *mg*	*Error mg*
Mg	50:1	30.3	0.1
Ca	50:1	29.7	−0.5
Sr	50:1	30.5	0.3
Ba	50:1	29.8	−0.4
Al	50:1	29.9	−0.3
Zn	50:1	29.6	−0.6
Cd	50:1	30.4	0.2
Hg(II)	50:1	30.6	0.4
Cu(II)	50:1	29.9	−0.3
Co(II)	2:1	30.0	−0.2
Ti(IV)	50:1	30.7	0.5
Cr(III)	2:1	30.5	0.3
Be	50:1	29.7	−0.5
Mn(II)	50:1	30.8	0.6
Ni(II)	50:1	29.9	−0.3
V(IV)	5:1	29.8	−0.4
Zr	5:1	Interferes	
Th	3:1	Interferes	
Bi	2:1	Interferes	

[a] Fe(III) taken = 30.2 mg.

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ANALYTICAL STUDIES WITH CDTMP

The metal chelates of CDTMP studied did not have the desired stabilities to allow the metals to be titrated with CDTMP using the common indicators. The single exception was iron(III), which could be titrated in acid solution.

Titration of iron(III)

It was possible to titrate iron(III) with CDTMP in a solution the pH of which was about 1.5. Sulfosalicylic acid was used as the indicator, and it was also found that the end-point was enhanced somewhat by the addition of a blue dye. At best, the end-point was poor and considerable practice was required to obtain reproducible results. The procedure developed for the titration of iron(III) was the following.

The sample to be titrated should be contained in a total volume of about 50 ml. The pH was adjusted between 1.0 and 1.5, and 0.5 ml (ten drops) of a 0.1 *M* solution of sulfosalicylic acid was added, followed by five drops of a 0.1% solution of indigo carmine or naphthol blue-black. The titration was carried out until no "flashes" of green were evident upon the addition of CDTMP. Table IX summarizes the titration of iron(III) in the presence of various cations. The significant interferences were thorium, zirconium, and bismuth. In each case a precipitate was formed during the course of the titration. Evidently this was some type of phosphonate of the metal in question. Of the common anions studied, only fluoride and phosphate interfered, and these prevented the formation of the iron(III)-sulfosalicylic acid complex. On the other hand, nitrate, sulfate, perchlorate, acetate, formate, bromate, chloride, and iodide caused no interference with the titration.

SUMMARY

The octasodium salt of N,N,N',N'-tetrakis-(phosphonomethyl)-1,2-cyclohexanediamine, Na_8-CDTMP, can be prepared in 45% yield from chloromethylphosphonic acid and 1,2-cyclohexanediamine. The titration curve resulting from the titration of the acid, CDTMP, with sodium hydroxide at 25° and $\mu = 0.1$ was used to estimate the eight pK values for the free acid. The stability constants of metal chelates of CDTMP were measured at 25° and $\mu = 0.1$ potentiometrically.

RÉSUMÉ

Le sel de sodium du N,N,N',N'-tétrakis-(phosphonométhyl)-diamino-1,2-cyclohexane a été préparé à partir de l'acide chlorométhylphosphonique et du diamino-1,2-cyclohexane. On a déterminé les constantes de dissociation et les constantes de stabilité des chélates de ce composé avec divers métaux.

ZUSAMMENFASSUNG

Es wird die Herstellung des Natriumsalzes des N,N,N',N'-Tetrakis-(methylphosphin)-1,2-diaminocyclohexans aus Chlormethylphosphinsäure und 1,2-Diaminocyclohexan beschrieben. Ferner wurden die Dissociationskonstanten der freien Säure sowie die Stabilitätskonstanten einer Reihe Metall-Chelate bestimmt.

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HIGH PRECISION TITRIMETRY*

I. AN EXAMINATION OF THE ATTAINABLE PRECISION

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Many excellent and meticulous examinations of factors influencing the precision of titrimetric operations have appeared in the past[1], though these are mainly 30 or more years old. In the present paper the accumulated observations of many years are offered in the form of a critical reassessment of the mechanical precision of normal titrimetric operations, an investigation of the maximum attainable mechanical precision, and some suggestions for improving replicability. It was hoped to establish whether or not there existed an ultimate limit to the precision, and therefore accuracy, of analytical processes, beyond which increase in mechanical precision of measurement brought no improvement in the chemical accuracy. The relevance of this to the chemical determination of atomic weights will be appreciated.

The accuracy and precision of routine volumetry and gravimetry are of the same order, roughly 0.1 to 0.5%. An increase of half an order is perhaps a little easier to achieve gravimetrically than volumetrically, but further increase calls for considerable refinement in both techniques, the advantage lying with volumetric or weight titrimetric methods. Protest must be maintained against the practice of reporting results to an excessive degree of accuracy. Though the precision (reproducibility) of the results, and the degree of fineness of measurement, may be good, the accuracy is often more apparent than real. Endeavours to improve or investigate the accuracy of a method by systematic examination of the factors involved often result initially in an apparent reduction in accuracy owing to removal of a previously compensating error. Attempts to improve the accuracy to the limits of mechanical precision of measurement are often defeated by physico-chemical limitations such as adsorption, equilibrium lability, non-stoichiometry, purity of materials and etc.

It is instructive to consider the mechanical limitations of the measurements. This inquiry relates not to routine work, but to titrimetric investigations into quantitativeness of reactions, and other problems which demand the highest degree of precision which the skill of the operator and the available instruments will allow.

INSTRUMENTS

Burettes

Normally the severest limitation is set by the burette, and more attention has properly been paid to improving precision in burettes than in other vessels. The ordinary burette cannot be read to better than ± 0.2%, but the best types with very fine ring graduations and well-made taps give setting errors of less than 0.005 ml (with very thin graduation lines) and reading errors of 0.01 ml, giving, with care and practice, a precision of 0.04%.

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* Paper read at the Symposium on Analytical Chemistry held by the Midlands Society for Analytical Chemistry at Birmingham in August 1954.

Many aids have been proposed for facilitation of reading and minimisation of parallax[2-5]; the card with a black line on it and a small piece of mirror held behind the burette are simple and good. The increased precision of sausage and bulb burettes (*e.g.*, B.S. 846) or EISSNER's double burette[6] is useful. The tap is often the weakest point, requiring lubrication and not being susceptible of minute manipulation. Most taps require initial seating by grinding with fine abrasive, and all should be reground from time to time.

Although lubrication is objectionable, pure white petroleum jelly has been found to be the least objectionable lubricant, and if the tap is manipulated gently, relubrication is needed only when the burette is cleaned. Silicone greases should be avoided because they spread rapidly over the internal surface of the burette, and are extremely difficult to remove. Lubrication by the titrant is applicable to needle valves in weight burettes[7], but not readily to volume burettes.

Delicacy of manipulation can be enhanced by extending one wing of the tap. A piece of stout, but light wire (aluminium tubing is excellent), glass tube, or shaped wood is attached to the tap, wired and sealed with sealing wax as shown in Fig. 1. Attachment of a plastic protractor card facilitates resetting to given delivery speeds. With a properly ground jet tip, very lightly waxed, extremely small drops can be formed, removed by touching the inside wall of the titration vessel or by a glass rod, and washed down.

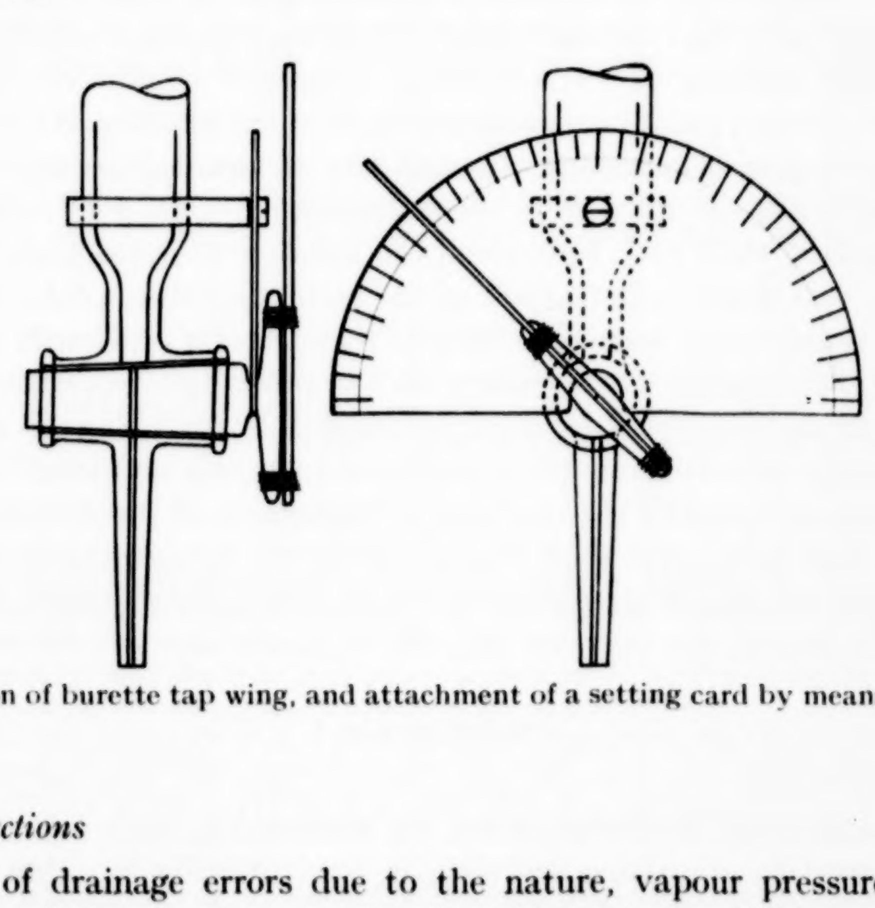

Fig. 1. Extension of burette tap wing, and attachment of a setting card by means of a Terry clip.

Drainage corrections

Variability of drainage errors due to the nature, vapour pressure and surface tension of the solution is of a second order of importance. With a perfectly clean burette and grease-free solutions, the error can be made remarkably uniform, thus permitting the application of a predetermined correction. The correction is much more dependent on delivery time than on drainage time. Drainage does not start immediately the outflow ceases; liquid builds up some 3–4 mm above the meniscus. This delay period becomes longer, and drainage becomes less, the slower the speed of delivery.

For a particular 50-ml burette, whose drainages are shown in Fig. 2, these factors became uniform at a delivery time of 6 min or longer, and a mathematical expression for drainage correction became possible:

$$\text{Drainage (ml)} = 0.2 \log_{10} \frac{\text{drainage time (min)}}{4[\text{delivery time (min)} - 3]}$$

Below 6 min, the relationship between delivery and delay times was no longer linear. The resemblance to the figures of LINDNER AND HASLWANTER[8] might suggest the universal application of the above expression, but the likeness must be ascribed to the accident of similar characteristics in the burettes used.

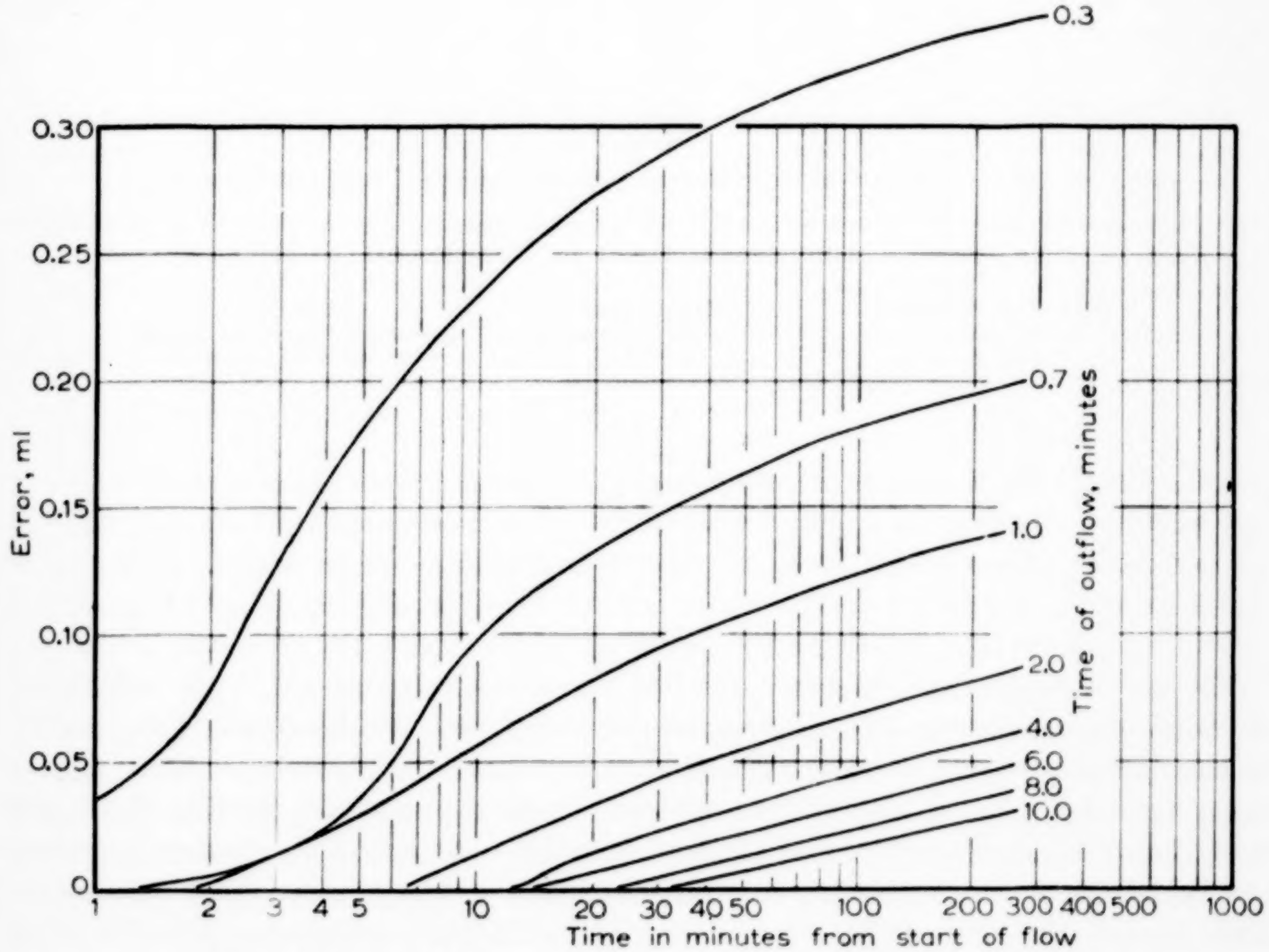

Fig. 2. Drainage of a 50-ml burette after various times of outflow.

With titrations of short duration, as in visual indicator or rapid electrometric working, no correction is necessary if the delivery speed is less than 8 ml per min, and the titration is completed within the delay period (the denominator of the above expression). With long titrations, as in careful plotting of potentiometric curves, when results have to be co-ordinated with rapid titrations, as in a study of indicator errors or quantitativeness of reactions, a correction corresponding to delivery speed and total time of titration may be taken from a drainage graph and either subtracted from the value for rapid titration, or, more properly, added to the figure for slow titration. If a burette is always used at the same delivery speed, a single, readily constructed drainage curve will suffice.

Since the delivery time at which uniformity begins is about three times as long as the "free delivery" time, on which standards institutions base their calibrations, recalibration at the new delivery time is necessary.

Errors due to inadequate rinsing are connected with drainage. Strongly held water films are not quickly replaced by the rinsing solution, and simple emptying by inversion leaves surprisingly large volumes of liquid behind. Large errors are incurred by the common practice of quickly rinsing a burette (or pipette) three times with 10–15 ml of solution and rapidly emptying between. Adequate drainage of 2–3 min between rinsings is important, and for the most accurate working the burette should be filled with solution after rinsing, allowed to stand 20–30 min, drained and refilled before commencing work. Table I shows the effect of this error in bromate–hydrazine titrations.

TABLE I

TITRATION OF 0.025M HYDRAZINE SULPHATE WITH 0.01667M POTASSIUM BROMATE

The titration was carried out in a solution 1.0M in hydrochloric acid and 0.1M in potassium bromide, using rosaniline hydrochloride as indicator. Theoretical end-point 24.52 ml.

Burette rinsed quickly 3 times without drainage	*Burette rinsed 3 times with intervening drainage*	*Burette rinsed 4 times with intervening drainage, and conditioned with solution*
24.63	24.55	24.52
24.65	24.52	24.52
24.70	24.54	24.515
24.58	24.56	24.52

The use of grease- and dust-free distilled water is a valuable aid in the reduction of errors. An automatic, self-cleaning, all-glass still, free of lubricated joints is used in this laboratory, the distillate filtered through porosity 3 sintered silica, stored in preconditioned bottles, and dispensed from a tapless apparatus. Moulds, algae and bacteria are also excluded by this method. A surface allowed to dry becomes greasy quickly, and a burette left empty overnight requires cleaning every 2 to 3 days. Slow alteration of the glass surface due to cleaning with such reagents as chromic acid demands that cleaning should be kept to a minimum. Frequency and duration of cleaning can be reduced by wet storage. A burette left completely filled with distilled water and covered with an inverted tube will remain clean when in daily use for 3 weeks or more, and if simply stored will remain clean for 3 or 4 months. Errors due to evaporation from a burette covered with an empty tube are small. Under very dry conditions, for dilute solutions at 20° evaporation is 0.002 ml/h for a full 50 ml burette, decreasing to about one twentieth of this as the burette is emptied. With ethanolic solutions[9], the loss from a covered burette is 0.03 ml/h when full, and 0.001 ml/h when nearly empty.

Pipettes

Pipettes are really precision instruments as the figures in Table II show. The above remarks on incomplete rinsing of burettes apply equally well to pipettes, thorough drainage between each of four rinsings being required.

TABLE II

WEIGHT OF WATER IN g DELIVERED BY PIPETTES AT 20°

Nominal volume, ml	*2*	*5*	*10*	*20*	*25*	*50*	*100*
Method (a)	1.983	4.993	9.984	19.964	25.008	49.892	99.771
	1.982	4.993	9.982	19.961	25.003	49.895	99.768
	1.981	4.995	9.985	19.963	25.005	49.892	99.773
Maximum scatter	0.002	0.002	0.003	0.003	0.005	0.003	0.005
Method (b)	1.9993	4.9955	9.9891	19.9777	24.9880	49.9226	99.8024
	1.9998	4.9953	9.9893	19.9776	24.9882	49.9229	99.8030
	1.9993	4.9956	9.9889	19.9780	24.9881	49.9220	99.8027
	1.9997	4.9954	9.9890	19.9778	24.9879	49.9224	99.8025
Maximum scatter	0.0005	0.0003	0.0004	0.0004	0.0003	0.0009	0.0006
Method (c)					24.9880		
					24.9881		
					24.9882		
					24.9880		
Maximum scatter					0.0002		

In method (a) student-type (class 'B') pipettes were held vertically by hand, suction applied by mouth, adjustment to the calibration mark made with the pipette tip, after wiping, touching the outer glass surface of a vessel, and delivery with the tip touching the inner surface of the receiving vessel, a timed interval of 15 sec being allowed after visible outflow ceased. The pipette was then withdrawn and the vessel weighed.

In method (b) standard class 'A' pipettes were used, clamped vertically, fitted with reading cards, and suction applied from a vacuum line *via* a two-way tap, whose other way was open to the air. After wiping the jet, adjustment to the calibration mark was made with the jet touching a glass surface. Free delivery was allowed with the jet touching the inner surface of the receiving vessel and a timed interval of 15 sec given after visible outflow ceased. The vessel was withdrawn from the pipette and weighed.

In method (c) the pipette was enclosed in a wide glass tubing water jacket connected to a thermostat tank, and water at the standard temperature circulated. Otherwise the method was similar to (b).

Many methods of using pipettes have been proposed from time to time, and a number of calibrations of a single pipette by a selection of these methods is shown in Table III. In methods 2, 4 and 6, the slight uncertainty of determining the point at which outflow ceases, together with the rapid drainage at this point, causes a considerable scatter of the results. The duration of the touch in 2, 3, 4 and 5 is open to various interpretations — about 1 sec was used — and gives variable errors.

TABLE III

WEIGHT OF WATER DELIVERED BY A NOMINAL 25 ml CLASS A PIPETTE OF OUTFLOW TIME 32 sec BY VARIOUS METHODS

Method	*1*	*2*	*3*	*4*	*5*
	24.866	24.884	24.982	24.890	24.972
	24.902	24.908	24.962	24.922	24.961
	24.872	24.924	24.970	24.913	24.985
	24.884	24.916	24.976	24.935	24.982
Mean	24.881	24.908	24.970	24.915	24.975
Maximum scatter	0.036	0.040	0.020	0.045	0.024

Method	*6*	*7*	*8*	*9*
	24.919	24.986	24.9880	24.9880
	24.930	24.984	24.9882	24.9881
	24.941	24.989	24.9881	24.9882
	24.934	24.988	24.9879	24.9880
Mean	24.931	24.987	24.9881	24.9881
Maximum scatter	0.022	0.005	0.0003	0.0002

Method 1. Free outflow without touching wall of vessel.
2. Free outflow without touching wall of vessel during outflow, but touch wall once as soon as outflow ceases.
3. As in 2, but wait 15 sec before touching wall.
4. As in 2, but touch liquid surface instead of wall.
5. As in 4, but wait 15 sec before touching liquid.
6. Free outflow touching wall of vessel. No drainage allowed after outflow ceases.
7. Method (a) of Table II.
8. Method (b) of Table II.
9. Method (c) of Table II.

Storage of pipettes completely immersed in water in covered cylinders increases the intervals between cleaning, but manually manipulated pipettes do get dirty rather quickly. Mechanical handling as in Methods (b) and (c) above allows their use for 3 to 4 weeks between cleaning, despite the presence of a lubricated tap in the air line.

Flasks

The principal limitation resides in the diameter of the neck, which must be large enough to permit good mixing, but narrow enough to minimise setting errors. With the greatest care the setting error may be as little as 0.03 ml on a 1-l flask and 0.01 ml on a 100-ml flask, but is normally much higher than this, being usually 0.02 to 0.04% with care, or slightly better than the burette.

PROCEDURES

Weighing

For ordinary work, weighing errors are negligible, reagent purity not justifying further refinement, though a vacuum correction accounts for roughly 1 mg/ml of material. However, when a 1-g sample is weighed to 4 places the error is 0.02%, the same as the burette error. Weighing errors can be made very small with extreme care and adequate balances and weights.

Application of corrections

Measurements so made still require correction for temperature, pressure and humidity. Such corrections are well-known and fully worked out for dilute aqueous solutions, but are seldom applied. This omission is made on the grounds that if conditions are uniform the corrections cancel out, and this is often justified, though caution is necessary. Fully to correct a series of determinations for all sources of known errors of measurement is very troublesome. With electrometric titrations of some duration, conducted while room temperature is rising, temperature corrections become very complicated. With non-aqueous solutions, the corrections are seldom known.

Many errors are negligible compared with the burette errors, though their cumulative effect may have significance; such factors as, *e.g.*, pressure variation requiring a correction of 0.002% per cm, which are normally ignored, call for correction in the most precise work. These corrections, and the calibration of weights and vessels are themselves subject to errors, and the sigmoid may easily assume alarming proportions unless extreme care is taken.

Weight titrimetric methods

Many corrections are eliminated by the use of weight titrimetric methods. It is surprising that these are not more used for precise work in these days of rapid weighing balances.

Preparation of solutions by weight instead of by volume eliminates errors due to thermal expansion of glass and solution. In weight titrations, errors of drainage, reading and temperature change are eliminated. Only the usual vacuum weighing correction is required.

Weight titrimetry introduces one error of its own; adsorption of moisture on the glass surfaces. This, unfortunately, is an indeterminate and often considerable error. A second disadvantage is that a large set of accurate weights is needed.

The titrations may be carried out in two ways.

(1) Direct titration by visual indicator or electrometric methods to the end-point and weighing the burette before and after.

(2) Titration to near the end-point, when the burette is re-weighed, and the titration finished volumetrically using a suitably diluted solution prepared volumetrically.

The second method is often more convenient in plotting titration curves, but there is little to choose between them in precision and accuracy.

By this method the precision in routine working can readily be enhanced one order,

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from 0.2 to 0.02%, or twice the best precision of careful volumetric work. With very great care, the precision can be brought up to just better than 0.01%.

Further to increase precision presents rapidly mounting difficulties, not the least being the detection of the end-point and reagent purity. At about this stage precision of measurement begins to exceed the precision of the process. Two suggestions are offered, one for ready improvement of the precision of normal volumetric processes, the other[7] to push the precision of titrimetric measurements to the limit.

The pipette-dilution method

Table II illustrates the high precision attainable with an ordinary pipette. With care, a reproducibility of 0.001 ml is attainable, and this may profitably be utilised. A pipette may be used to deliver (after the manner of a weight burette in method (2) above) the bulk of the titrant, to within 0.25 or 0.025 ml before the end-point, and the titration completed with a 10- or 100-fold dilution of the original solution. This has proved particularly useful in investigating the end-point region in potentiometric curves.

This is reaching the limit of most indicators, even sharpened by photoelectric detection, and most electrometric techniques. It is also on the limit of reagent purity. Further increase in precision of measurement does not improve the reproducibility of the results.

TABLE IV

TITRATION OF 0.1 M FERROCYANIDE WITH 0.1 M CERATE IN 1 M SULPHURIC ACID, USING VICTORIA GREEN AS INDICATOR

Method	*Careful direct volumetric visual end-point*	*Pipette dilution visual end-point*	*Pipette dilution photoelectric end-point*
Readings	24.98	24.984	24.983
	24.98	24.982	24.985
	24.99	24.984	24.984
	24.98	24.988	24.984
Scatter	0.01	0.006	0.002
Precision	0.04%	0.024%	0.008%
Method	*Direct weight-volumetric visual end-point*	*Dilution weight-volumetric visual end-point*	*Dilution weight-volumetric photoelectric end-point*
Readings	24.9816	24.9831	24.9833
	24.9845	24.9892	24.9839
	24.9898	24.9860	24.9854
	24.9837	24.9838	24.9842
Scatter	0.0082	0.0061	0.0021
Precision	0.033%	0.024%	0.0085%

Table IV shows that the pipette-dilution method increases the precision of the results in titration with a colour indicator to a visual end-point by allowing a further decimal place to be read. This improvement is small because the limit of visual discrimination of colour has been reached. With photoelectric detection of the end-point, the extra precision of measurement becomes effective, and there is an improvement in reproducibility of results. On increasing the mechanical precision another order by weight titration, weighing to four places, the reproducibility of the results, either by visual or photoelectric detection of the end-point, is in no way improved. In the direct titration, increase of mechanical precision by two full orders by weighing instead of reading a burette yields hardly any improvement in reproducibility. The results of weight titrations have been converted to volumes for direct comparison.

CONCLUSION

With a proper appreciation of the mechanical errors of titrimetric measurements and adequate care in manipulative technique to take account of these, the precision and accuracy of the results of titrimetric determinations can readily be made commensurate with the precision of discrimination of end-point and the limits of normal reagent purity. Increase of mechanical precision beyond this affords no increase in the precision of the results.

ACKNOWLEDGEMENTS

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SUMMARY

A re-examination and critical assessment of the mechanical precision of titrimetric processes, with particular reference to the drainage errors of burettes, has been made and some manipulative improvements suggested.

The pipette-dilution method offers a useful improvement in the precision of volumetric methods, but further increase in mechanical precision affords little or no improvement in accuracy of determination.

RÉSUMÉ

La précision mécanique des méthodes titrimétriques est soumise à un nouvel examen critique, en particulier en vue des erreurs dues à l'écoulement des burettes. On constate que la précision des méthodes volumétriques peut être augmentée en se servant de pipettes et de solutions diluées pour la fin du titrage.

ZUSAMMENFASSUNG

Die mechanische Genauigkeit der titrimetrischen Verfahren wird aufs Neue kritisch untersucht, und zwar unter besonderer Berücksichtigung der Ausflussfehler der Büretten. Er wurde festgestellt, dass man durch Verwendung von Pipetten und von verdünnten Lösungen am Ende der Bestimmung, die Genauigkeit der volumetrischen Methoden erhöhen kann.

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THE CHELOMETRIC DETERMINATION OF CHROMIUM, COBALT(III) AND COPPER WITH A METALFLUORECHROMIC INDICATOR

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The successful application of calcein as a metalfluorechromic indicator for the determination of cobalt and iron[1] indicated that similar success would be attained with other highly colored EDTA–metal complexes. For this reason a study was initiated on the determination of chromium, cobalt(III) and copper. These elements form highly colored complexes with EDTA which cause considerable difficulty in their determination.

The determination of chromium is always conducted as a back titration because of the slow reaction between EDTA and chromium[2]. The titration using visual indicators is limited to relatively small amounts of chromium.

The titration of trivalent cobalt is seldom used due to the intense color of the EDTA–cobalt(III) complex. The determination of small amounts has been carried out by a back titration of an excess of EDTA using thorium as a titrant and xylenol orange as an indicator[3]. The cobalt(III)–EDTA complex is formed in ammoniacal solution by oxidation with hydrogen peroxide. The solution is subsequently acidified (pH = 2) and back titrated with thorium. The back titration of cobalt(III) in ammoniacal solution presents an additional difficulty in that most of the indicators used in ammoniacal solutions are sensitive to oxidizing agents.

The preliminary experiments were confined to ascertaining if calcein would function in ammoniacal solution in the presence of hydrogen peroxide. Several titrations of an EDTA solution at pH of 9.5 were conducted in the presence of hydrogen peroxide. The values obtained could not be distinguished from those in the absence of hydrogen peroxide.

PROCEDURES

Cobalt

A cobalt solution is adjusted to a pH of 9.5 with ammonium chloride–ammonium hydroxide buffer and somewhat more than the equivalent amount of EDTA is added. The volume is adjusted to approximately 150 ml, one drop of calcein (0.1% in 0.001 *N* NaOH) is added and the solution back titrated under ultraviolet illumination with a standard copper solution. The equivalence point is characterized by the quenching of the brilliant green fluorescence of the indicator.

Chromium

To a slightly acidic solution of chromium add somewhat more than the equivalent amount of EDTA. Adjust the pH to 4.5 with sodium acetate–acetic acid buffer and dilute to approximately 150 ml with distilled water. Boil the solution for about 15 min, add one drop of calcein indicator and back titrate with a standard copper solution under ultraviolet illumination. The end-point is characterized by the quenching of the fluorescence of the free indicator.

Copper

Add somewhat more than the equivalent amount of EDTA to a copper solution which is buffered at a pH between 4.5 and 9.5. Dilute to approximately 150 ml, add one drop of calcein and back titrate with a standard copper solution to the quenching of the fluorescence of the free indicator.

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DISCUSSION

The back titrations with standard copper solution are most conveniently carried out with ultraviolet light as the sole source of illumination. A convenient apparatus for this titration has been previously described[1]. The fluorescent radiation of the indicator before the end-point provides adequate illumination of the buret tip so as to make dropwise addition of the titrant feasible.

The titration of relatively large amounts of cobalt, chromium and copper by the methods described above are presented in Table I. It is apparent that the color of the EDTA–metal complexes does not interfere in the titration.

The possibility of determining the end-point in the presence of large amounts of copper is particularly advantageous. If an unusually large excess of EDTA is inadvertently added to a sample prior to a back titration with standard copper, the EDTA–copper complex formed during the back titration does not interfere with the titration.

TABLE I

DETERMINATION OF COBALT, CHROMIUM AND COPPER USING CALCEIN

Sample No.	*mg Co added*	*mg Co found*	*Sample No.*	*mg Cr added*	*mg Cr found*	*Sample No.*	*mg Cu added*	*mg Cu found*
1	21.25	21.20	12	20.00	19.97	23	47.65	47.61
2	21.25	21.23	13	20.00	19.89	24	47.65	47.60
3	42.50	42.47	14	20.00	19.99	25	47.65	47.64
4	42.50	42.52	15	20.00	19.97	26	47.65	47.66
5	42.50	42.56	16	40.00	39.98	27	47.65	47.63
6	42.50	42.52	17	40.00	39.87	28	47.65	47.67
7	63.75	63.88	18	40.00	40.06	29	47.65	47.67
8	63.75	63.79	19	40.00	40.03	30	47.65	47.65
9	63.75	63.70	20	40.00	39.97	31	57.18	57.16
10	63.75	63.86	21	40.00	40.12	32	57.18	57.21
11	63.75	63.70	22	40.00	39.95	33	57.18	57.20

SUMMARY

Calcein has been applied as a metalfluorechromic indicator for the back titration of relatively large amounts of cobalt(III), chromium(III) and copper(II). The fluorescent end-point is not impaired by the presence of the highly colored EDTA complexes with these ions. Calcein is suitable as an indicator which is not sensitive to oxidation in alkaline solutions.

RÉSUMÉ

La calcéine est proposée comme indicateur de fluorescence pour le titrage indirect de relativement fortes teneurs de cobalt, de chrome et de cuivre.

ZUSAMMENFASSUNG

Calcein wird als Fluoreszenz-Indikator für die indirekte Titration relativ grosser Mengen von Kobalt, Chrom und Kupfer vorgeschlagen.

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THE IODIMETRIC DETERMINATION OF THE REDUCING CAPACITY OF ALUMINIUM ALKYLS

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INTRODUCTION

Aluminium alkyls are used as catalysts in various chemical reactions. An important characteristic of this catalyst is its reducing capacity. This analytical method was developed to enable rapid and accurate determination of the total empirical reducing capacity of such a catalyst in concentration units of normality.

The procedure does not differentiate between aluminium alkyls, aluminium alkoxides, or aluminium hydrides.

OUTLINE OF METHOD

When aluminium alkyl comes into contact with an oxidizing agent, air, or water, a vigorous reaction results with the aluminium generally forming an inorganic salt or oxide and the alkyl usually going to a hydrocarbon or a halide. If this reaction goes to completion, one mole of triethyl aluminium will give up three electrons. However, depending on the strength and concentration of the oxidizing agent, diverse side reactions can take place. By careful control of the reaction conditions, the side reactions can be kept to a minimum.

To determine the reducing capacity of aluminium alkyl, an aliquot of the sample is added to a solution of iodine and potassium iodide in benzene.

The reactions taking place are as follows:

$$1.\ \mathrm{Al(C_2H_5)_3 + 3I_2 \rightarrow AlI_3 + 3C_2H_5I}$$

$$2.\ \mathrm{I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI}$$

Apparatus

The glass bomb used for sampling the aluminium trialkyl is shown in Fig. 1.

Reagents

Standard iodine solution. Dissolve 51 g of resublimed iodine in 1 l of benzene. Standardize against standard sodium thiosulfate.

Benzene. Dry over $Mg(ClO_4)_2$ for at least 1 day.

Standard sodium thiosulfate solution, 0.2*N*. Dissolve 31.6 of reagent-grade sodium thiosulfate in 1 l of boiled and cooled, deionised water. Standardize against 0.1*N* potassium iodate solution. (Use any standard text book procedure.)

Potassium iodide. Dry, reagent grade.

Glacial acetic acid. Reagent grade, dry.

Nitrogen. Pass over Drierite, heated copper turning, and Drierite again to eliminate water and oxygen.

Sampling

Flush sample bomb with dry, oxygen-free nitrogen. Attach the bomb to the sample source, avoiding contamination with air or moisture. Open all valves and allow a suitable sample to flow into the bomb. Close all valves, beginning with the one on the sample source.

Preparation of apparatus

All the equipment used should be *thoroughly cleaned and dried*. All stopcocks and joints should be greased with Apiezon grease or high vacuum silicone grease. After assembling the apparatus, flush the entire assembly with dry, oxygen-free nitrogen for 10 to 15 min to remove moisture and air. Close all stopcocks.

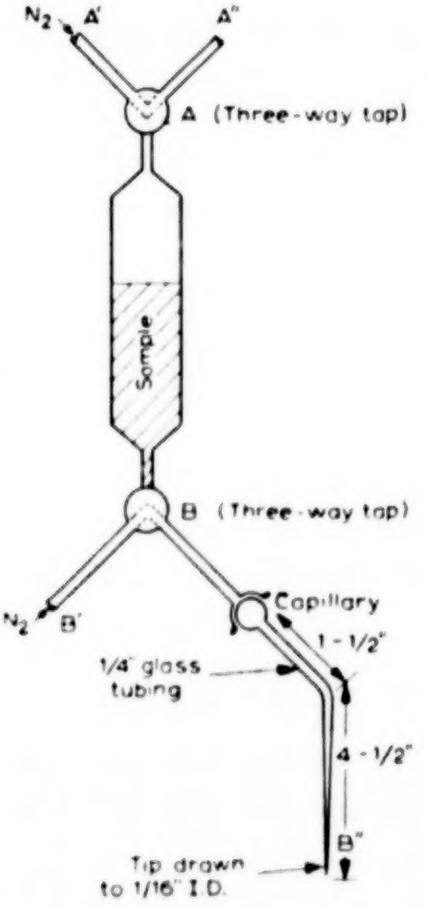

Fig. 1. Sample bomb.

Recommended procedure

Note: Use dry, oxygen-free nitrogen in all cases.

1. Prepare reaction beaker as follows: To a 100 ml, tall-form beaker add 25 ml of standard iodine solution plus 2 g of potassium iodide. Place a cover glass over the top of the beaker. The cover glass is made with three small holes to allow (a) the capillary inlet, (b) nitrogen inlet, and (c) burette inlet for titration. Flush with nitrogen to remove any dissolved oxygen and to form an inert blanket over the reaction vessel. Stir contents of beaker at a suitable rate on a magnetic stirrer.
2. Weigh sample bomb and sample.
3. Affix capillary tip.
4. Adjust nitrogen pressure to 2.5 ψ.
5. Connect nitrogen to taps A and B.
6. Turn taps A and B to allow passage from A′ to A″ and B′ to B″, respectively. Sweep out all tubing, capillary, and tip with nitrogen (see Fig. 1).

7. Immerse capillary tip below surface of reaction solution.
8. Run in a suitable sample by opening taps A and B and displacing with nitrogen.
9. Reweigh sample bomb plus remaining sample.
10. Add 5 ml of glacial acetic acid to reaction vessel.
11. Titrate with standard thiosulfate in the normal fashion using starch as an indicator.

The time taken to complete an analysis is approximately 30 min.

Calculations

Calculate the normality of the alkyl catalyst by the following equation:

$$\frac{(V_1 \times N_1) - (V_2 \times N_2)}{V_3} = N_3$$

Wt. of sample =
(wt. sample bomb + sample) — (wt. sample bomb + remaining sample)
V_1 = Volume of benzene-iodine solution
N_1 = Normality of benzene-iodine solution
V_2 = Vol. of sodium thiosulfate
N_2 = Normality of sodium thiosulfate
V_3 = Vol. of triethyl aluminium sample = wt. sample ÷ density*
N_3 = Reducing strength of triethyl aluminium expressed as normality.

Blank

If desired, a blank determination may be carried out on the solvent used to slurry the alkyl and the analytical results corrected in the normal way.

Precision

The following short term precision data have been obtained:

	Normality
	0.0625
	0.0626
	0.0627
	0.0625
	0.0628
	0.0629
	0.0629
	0.0630
	0.0632
Avg. =	0.0628
2σ =	0.00048 (95% confidence)

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* The density is considered to be the same as that of the solvent for low concentration slurries normally encountered.

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DISCUSSION

The aluminium alkyls react instantaneously with air and moisture; the delivery tip of the burette may therefore become clogged at times with reacted alkyl. This will necessitate periodically cleaning the delivery tip with a fine wire. To keep clogging to a minimum, it should be thoroughly dried after each analysis and especially before leaving overnight.

Since iodine is volatile, KI is added to the iodine-benzene system to prevent the loss of I_2 by binding it as the I_3^- complex. The addition of KI also greatly increases the solubility of I_2 in water and gives a better end-point to the titration.

Glacial acetic acid is added in excess to the reaction mixture to prevent undesirable side reactions. The formation of sulfate, which would give high results, is retarded in an acidic medium.

The reaction of the aluminium alkyl catalyst with iodine also appears to be subject to side reactions. This is largely overcome by using a fourfold excess of iodine in respect to the alkyl concentration.

Reasonably good precision was obtained in practice if the proper steps were taken to prevent contact with air. It was also found desirable to analyse samples within a few hours, otherwise traces of air leaked into the sample bomb.

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to J. L. JONES and Mrs. J. ELLERBE for their help and suggestions in completing this project; also, to Esso Standard Oil Company for permission to publish this paper.

SUMMARY

A rapid method for the determination of the reducing strength of aluminium alkyls has been developed. The method depends on the reaction with iodine. Replicate analysis shows a reasonable degree of precision.

RÉSUMÉ

Une méthode iodimétrique rapide est proposée pour déterminer le pouvoir réducteur des alcoylaluminiums.

ZUSAMMENFASSUNG

Es wird eine jodometrische Schnellmethode zur Bestimmung der Stärke der Reduktionswirkung von Aluminiumalkylen beschrieben.

REFERENCE

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DAS RUTIN ALS ANORGANISCH-ANALYTISCHES REAGENS

II. NACHWEIS VON VANADIUM(V) MIT RUTIN

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Als in unserer vorläufigen Mitteilung[1] gemeldet wurde, gibt das Rutin (Quercetin-3-rutinosid) mit verschiedenen Metallionen eine Farbreaktion, welche durch entsprechende Auswahl der Umstände für die einzelnen Metallionen weitgehend spezifisch gestaltet werden kann. In diesem Artikel möchten wir über die sehr einfache und empfindliche Nachweismethode von Vanadium(V) berichten.

Die Reaktion wurde von uns anfänglich an einer 40, später 18 μg/ml Vanadium(V) enthaltenden Lösung näher studiert. Die 10-mal grössere Konzentration der — mit verdünnter Schwefelsäure bereiteten — Stammlösung wurde permanganometrisch bestimmt.

Fügt man zu 1 ml NH_4VO_3 Lösung, 1 ml 0.5%-ige Rutinlösung in Methanol, dann 3 ml 82%-ige Phosphorsäurelösung, so erscheint eine wohl beobachtbare orangerote Farbe.

Die Empfindlichkeit der Farbreaktion lässt sich durch Ammoniumpersulfat erheblich erhöhen. Fügt man z.B. zu 1 ml der Lösung die zu untersuchen ist, 1 ml 10%-ige Ammoniumpersulfatlösung, 1 ml 0.5%-ige Rutinlösung in Methanol, dann 3 ml 82%-ige Phosphorsäurelösung, so sieht man die orangerote Farbreaktion auch noch in Gegenwart von 0.3 μg Vanadium(V) klar. Die Farbe ist von der schwach grünlichgelben Farbe der Blindprobe gut unterscheidbar.

Eine interessante Beobachtung, in Bezug auf die Geschwindigkeit der Reaktion besteht darin, dass mit frischer Lösung von Ammoniumpersulfat in Gegenwart von weniger als 10 μg Vanadium(V) die orangerote Farbe erst in einigen Minuten hervorkommt, mit einer 1-2 Monat alten Ammoniumpersulfatlösung erscheint sie aber auch bei ganz kleinen Vanadiummengen sofort. Die an der Hand liegende Vermutung, dass dabei eventuell Wasserstoffperoxyd eine Rolle spielt, hat sich als unrichtig erwiesen. Gibt man nämlich zu einer 18 μg/ml enthaltenden Vanadiumprobe sogar 1 ml 5%-iger H_2O_2 Lösung anstatt der Ammoniumpersulfatlösung, so erscheint die Orangefarbe auch nach 5 Minuten noch nicht.

Die Reaktion wird von den meisten Ionen nicht gestört, sie ist also weitgehend spezifisch. Bei dem Nachweis von 1 μg/ml Vanadium(V) stören selbst in 1000-facher (also 1 mg/ml) Konzentration die folgenden Ionen nicht: Li, Na, K, (NH_4), Mg, Ca, Sr, Zn, Cd, Hg(II), Al(III), La(III), Ce(III), Tl(I), Sn(II), Sn(IV), Th(IV), As(III), As(V), Sb(III), Sb(V), Mo(VI), W(VI), U(VI), Mn(II), Co(II), Ni(II), Cu(II), Cl^-, NO_3^-, SO_4^{-2}.

Bei der obigen Ausführung der Reaktion wirken aber mehr als 100 μg Fe(II), oder Fe(III), 15 μg Ti(IV), 40 μg Ce(IV) und 250 μg MnO_4^- Ionen störend. Mit der eigenen Farbe stört mehr als 180 μg Cr(III) auch.

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Die störende Wirkung von Fe(II) und Fe(III) ist leicht auszuschalten durch Zugabe von 2 ml 5%-igen Äthylendiamintetraessigsäures Natrium zur untersuchenden Lösung noch vor dem Rutin. In Gegenwart von Ti(IV) fügt man zur Lösung noch 2 ml 3%-ige NaF Lösung, dann verfährt man wie oben. Die störende Wirkung der Ce(IV) bzw. MnO_4^- Ionen ist am einfachsten so auszuschalten, dass man zur untersuchenden saueren Lösung 1–2 Tropfen H_2O_2 gibt, danach ist die Reaktion ohne Störung ausführbar. So stören, bei dem Nachweis von 1 μg/ml Vanadium(V), auch 1000-fache Mengen von den genannten Ionen nicht mehr.

Die Farbreaktion gründet sich nach unseren Erfahrungen auf der katalytischen Oxydation des Rutins durch das Vanadium(V).

DANK

Das Rutin wurde uns von Herrn Prof. Dr. R. Bognár und V. Szabó zur Verfügung gestellt. Wir möchten dafür auch an dieser Stelle unseren besten Dank aussprechen.

ZUSAMMENFASSUNG

Es wurde eine einfache, schnell ausführbare, empfindliche und weitgehend spezifische Methode zum Nachweis von Vanadium(V) ausgearbeitet. Das Wesen der Methode besteht in einer Farbreaktion des Vanadiums mit dem Rutin in Gegenwart von Ammoniumperoxydisulfat in phosphorsäurem Medium.

Nachweisgrenze: 0.3 μg Vanadium(V) in 1 ml Lösung.

SUMMARY

A simple, sensitive and highly specific test is presented for the detection of vanadium(V). The test is based on the color reaction of vanadium(V) with rutin (quercetin-3-rutinoside) in the presence of ammoniumperoxydisulfate in phosphoric acid.

Sensitivity: 0.3 μg vanadium(V) in 1 ml solution.

RÉSUMÉ

Une réaction simple, sensible et spécifique est proposée pour l'identification du vanadium. On effectue cet essai au moyen de rutine en présence de persulfate d'ammonium et d'acide phosphorique. On obtient une coloration rouge orange.

LITERATUR

[1] P. Szarvas, Z. Jarabin und L. Dede, *Magyar Kém. Folyóirat*, 63 (1957) 151.

Eingegangen den 15. September 1958

SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF COBALT, NICKEL AND COPPER WITH DITHIO-OXAMIDE

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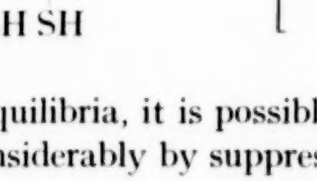
INTRODUCTION

Cobalt, nickel and copper are frequently used as alloying metals in steel, and copper and nickel are extensively used as alloying metals in aluminum.

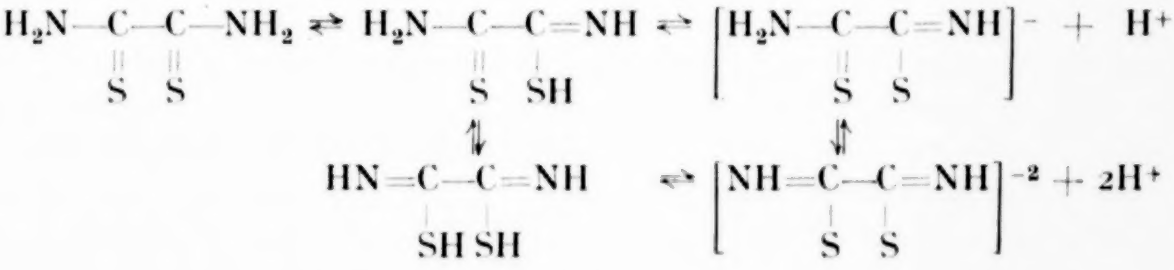
Since cobalt, nickel and copper are often found in the same substance, a method for the simultaneous determination of the three metals is of great practical importance. CHILTON[1] developed a simultaneous spectrophotometric method for cobalt, nickel and copper based upon the reactions of these ions with diethyldithiocarbamate and subsequent extraction of the complexes into carbon tetrachloride. This paper presents a simultaneous spectrophotometric method for the determination of cobalt, nickel and copper based upon the reactions of these ions with dithio-oxamide (rubeanic acid).

Dithio-oxamide or rubeanic acid has the following structure:



$$H_2N-\underset{\underset{S}{\|}}{C}-\underset{\underset{S}{\|}}{C}-NH_2.$$

In water–ethanol solutions, the following tautomerism and dissociation equilibria must be taken into account:



$$H_2N-\underset{\underset{S}{\|}}{C}-\underset{\underset{S}{\|}}{C}-NH_2 \rightleftarrows H_2N-\underset{\underset{S}{\|}}{C}-\underset{\underset{SH}{|}}{C}=NH \rightleftarrows \left[H_2N-\underset{\underset{S}{\|}}{C}-\underset{\underset{S}{|}}{C}=NH\right]^- + H^+$$

$$HN=\underset{\underset{SH}{|}}{C}-\underset{\underset{SH}{|}}{C}=NH \rightleftarrows \left[NH=\underset{\underset{S}{|}}{C}-\underset{\underset{S}{|}}{C}=NH\right]^{-2} + 2H^+$$

From a consideration of these equilibria, it is possible to increase the concentration of the dithio-oxamate anions considerably by suppressing or removing H^+ ions, *e.g.*, by addition of hydroxide ions.

RÂY[2] was the first to show that cobalt, nickel and copper can be precipitated quantitatively by dithio-oxamide from ammoniacal solution. Since then a number of investigators[3–13] have made studies primarily on the use of dithio-oxamide as a reagent for copper.

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APPARATUS

Spectrophotometers. Beckman spectrophotometers, Model DK-2 and Model DU, with 1-cm Corex cells were used.

pH Meter. A Beckman pH meter, Model G, was employed for all pH measurements. It was calibrated daily with Fisher Certified Standard Buffers.

REAGENTS

Standard cobalt solution. A solution containing 1 mg/ml cobalt was prepared by dissolving 2.03 g of cobalt chloride hexahydrate in doubly-distilled water. Twice distilled hydrochloric acid was added so that the final concentration, after dilution to 500 ml, was 1 *M*. The solution was standardized electrolytically.

Standard nickel solution. A standard nickel solution containing 1 mg/ml nickel was prepared by dissolving 2.03 g nickel chloride hexahydrate in the above manner. The solution was standardized by the dimethylglyoxime gravimetric method.

Standard copper solution. A copper solution containing 1 mg/ml copper was prepared by dissolving 1.45 g of cupric chloride dihydrate in the above manner. The solution was standardized electrolytically.

Buffer solutions. A pH 9 buffer was prepared by dissolving 3.84 g of sodium borate decahydrate in 1 l of doubly-distilled water and a pH 4 buffer by dissolving 1.01 g of potassium acid phthalate in 100 ml of doubly-distilled water. All other buffers were prepared according to the directions given by BRITTON[14].

Dithio-oxamide solution. A $1.5 \cdot 10^{-3} M$ solution of dithio-oxamide was prepared by dissolving 45 mg in 250 ml of absolute ethanol.

Gum acacia solution. A 0.1% solution of gum acacia was prepared by dissolving 0.2 g in 200 ml of doubly-distilled water.

Doubly-distilled water. All water used in this work was distilled twice and finally run through a cation exchange resin, Amberlite IR-120. The resin column was 26 cm in length and had an internal diameter of 2 cm.

Other reagents. All other reagents were analytical grade and were used without further purification.

EXPERIMENTAL

Properties of the reagent

Dithio-oxamide is an orange-red solid which is soluble in ethanol forming an orange colored solution. The absorbance curve for a $1.2 \cdot 10^{-4} M$ solution is shown in Fig. 1.

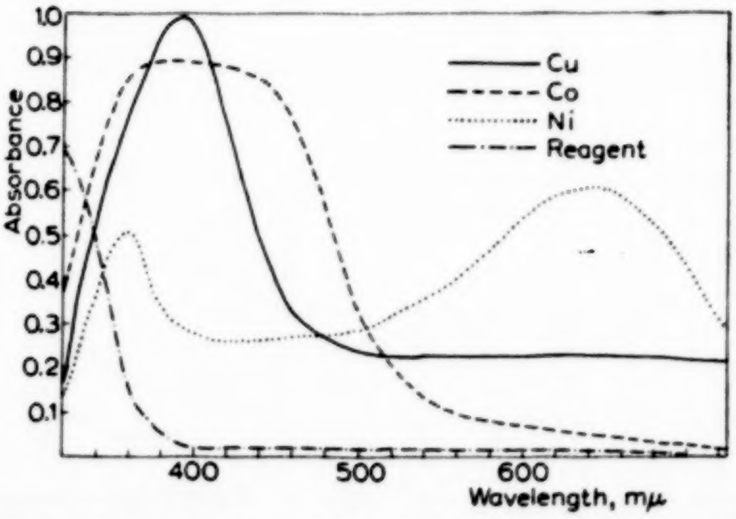

Fig. 1. Absorbance curves of 4.00 p.p.m. solutions of cobalt, nickel and copper; reagent curve, $1.2 \cdot 10^{-4} M$. All at pH 9.0 ± 0.3.

In order to cover the useful range of metal ion concentrations conveniently and to provide a sufficient excess of reagent, a $1.5 \cdot 10^{-3} M$ reagent solution was used.

The reagent solution is stable to light, hydrolysis, and oxygen and carbon dioxide of the air. Absorbance measurements on the reagent solution showed no significant change over a period of six weeks; measurements were not made over a longer period.

Properties of the complexes

Color. Cobalt, nickel and copper form water-insoluble complex salts with the reagent solution. The cobalt complex is yellow, the nickel complex blue and the copper complex olive green. A protective colloid such as gelatin or gum acacia keeps the complex in solution over the concentration range used. Gum acacia was used in this work in preference to gelatin because it is much more stable. Absorbance curves of 4.00 p.p.m. solutions of the complexes are shown in Fig. 1. The absorbances of the complexes were measured against a reagent blank. The nickel and copper complexes have a maximum at 640 $m\mu$ and 385 $m\mu$, respectively, while the cobalt complex has a broad absorbance peak with the maximum occurring at approximately 370 $m\mu$. At 440 $m\mu$ the absorbance of the cobalt complex is only about 3.5% less than at 370 $m\mu$. Since the absorbances of the reagent, the nickel complex and the copper complex are all less at 440 $m\mu$ than at 370 $m\mu$, the former is the most advantageous wavelength to use when simultaneous determinations are to be made.

Effect of pH. The effect of the hydrogen-ion concentration on the complexes is shown in Fig. 2. The absorbance curves were obtained by using 4.00 p.p.m. of the ion, 4 ml of a 0.1% gum acacia solution, 10 ml of a buffer solution of the desired pH and 3 ml of the reagent solution. The samples were diluted to 25 ml with distilled water and absorbance measurements made against a reagent blank. From the curves it is seen that the optimum pH for making simultaneous measurements is 9.0 ± 0.3.

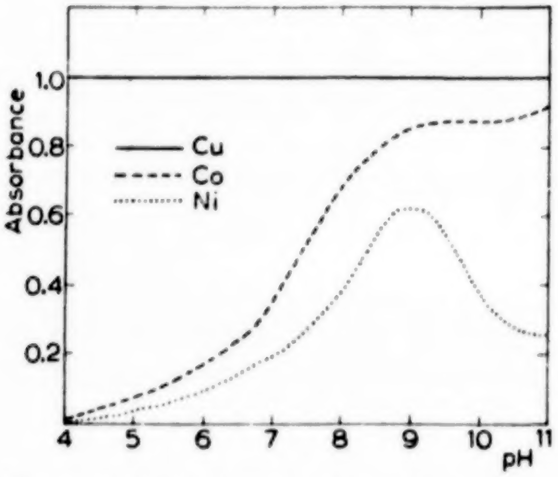

Fig. 2. Effect of pH on the cobalt, nickel and copper complexes.

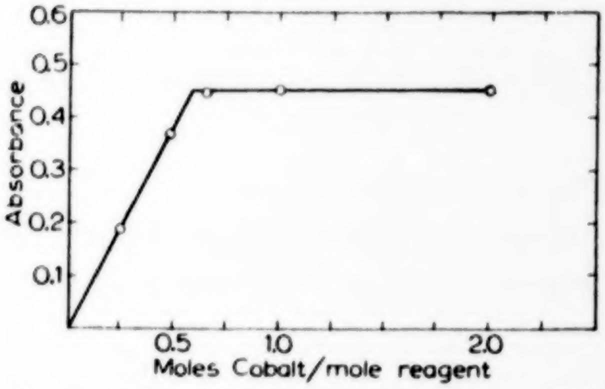

Fig. 3. Mole ratio method applied to cobalt complex.

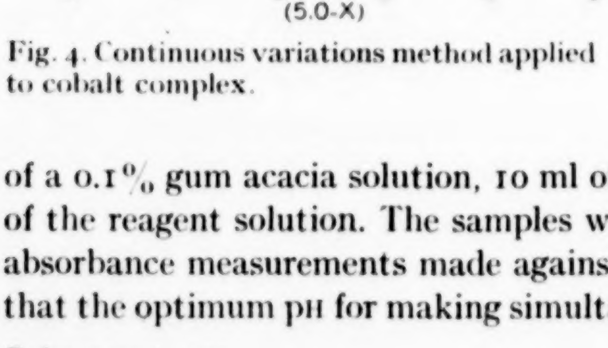

Fig. 4. Continuous variations method applied to cobalt complex.

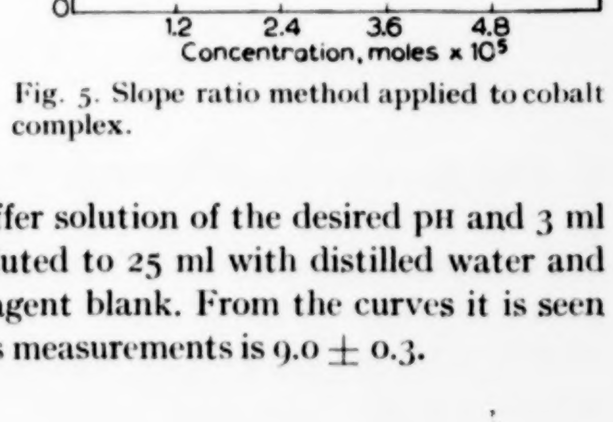

Fig. 5. Slope ratio method applied to cobalt complex.

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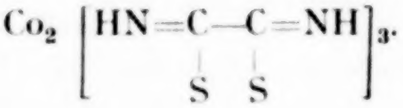
Structure of the complexes in solution. The empirical formulas of the three complexes *in solution* were established by three independent methods: the mole ratio method of YOE AND JONES[15], the continuous variations method of JOB as modified by VOSBURG AND COOPER[16], and the slope ratio method of HARVEY AND MANNING[17]. The results of these three methods applied to the cobalt complex are shown in Figs. 3, 4 and 5. They indicate a ratio of 2 moles of cobalt to 3 moles of reagent. This corresponds to a salt of Co^{+3} and reagent having a formula



$$Co_2\left[\begin{array}{c}HN{=}\underset{|}{\overset{}{C}}{-}\underset{|}{C}{=}NH\\ \quad S\quad S\end{array}\right]_3.$$

Nickel and copper both combine in ratios of 1 mole ion to 1 mole reagent indicating that salts are formed by Ni^{+2} and Cu^{+2} reacting with the divalent dithio-oxamate anion.

Order of addition of reagents. For maximum sensitivity the solutions containing the metallic ion and protective colloid must be adjusted to the proper pH before the reagent solution is added.

Effect of temperature. Temperature studies made at 15°, 25°, and 35° showed each of the complexes to be independent of normal variations in laboratory temperature.

Adherence to Beer's law. A series of samples containing varying concentrations of the metallic ion, 4 ml gum acacia solution, 10 ml of pH 9 buffer and 3 ml of reagent solution was prepared and diluted to 25 ml with distilled water. The absorbances of these solutions were measured against a reagent blank at wavelengths of 640 mμ for the nickel complex, 385 mμ for the copper complex, and at wavelengths of 440 mμ and 370 mμ in the case of the cobalt complex. Fig. 6 shows that Beer's law is obeyed by the cobalt complex at both wavelengths over the range 0.16 p.p.m. to 4.00 p.p.m. The complexes of nickel and copper follow Beer's law over the same concentration range. Lower and higher concentrations were not investigated.

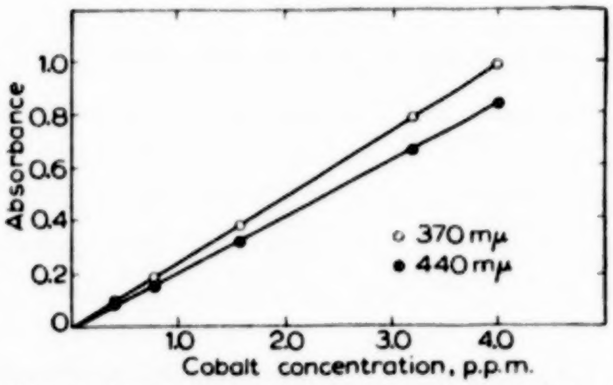


Fig. 6. Beer's law plot for cobalt complex.

Effect of diverse ions. The effect of foreign ions may be due to one of the following causes:

1. The foreign ion may react with the reagent.
2. The foreign ion may react with the ion to be determined.
3. The foreign ion may precipitate because of the pH of the solution.

The metal ions that react with dithio-oxamide in alkaline medium, exclusive of cobalt, nickel and copper, are palladium, silver, platinum, gold, mercury, and lead.

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These ions interfere with the determination of cobalt, nickel and copper when present in ratios of 1:1 or more. An interference was arbitrarily chosen as a change in absorbance of 0.010 unit, corresponding to 0.2 p.p.m. Co, 0.3 p.p.m. Ni and 0.2 p.p.m. Cu.

The cyanide ion must be absent since it forms more stable complexes with the three ions than does dithio-oxamide. High concentrations of citrate and tartrate ions, *i.e.*, concentrations high enough to prevent the precipitation of iron and aluminum at pH 9, interfere in the determination of cobalt and nickel but not in the determination of copper.

Ions such as Fe^{+3}, Al^{+3}, Mn^{+2}, etc. which precipitate in alkaline solution must be absent or, if present, must either be removed or complexed to prevent their interference.

Sensitivity. The sensitivities of the color reactions as defined by SANDELL[18] are as follows:

for cobalt at 440 mμ, 0.0046 γ/cm^2;
for nickel at 640 mμ, 0.0068 γ/cm^2;
for copper at 385 mμ, 0.0037 γ/cm^2.

Practical sensitivities, *i.e.*, an absorbance of 0.005 unit are: 0.023 p.p.m. Co, 0.034 p.p.m. Ni and 0.019 p.p.m. Cu.

Simultaneous determination of cobalt, nickel and copper

Table I lists the values of the molar extinction coefficients of the complexes of cobalt, nickel and copper measured at wavelengths of 440 mμ, 640 mμ and 385 mμ, respectively. These values may be used to calculate equations for the determination of one or more components[19]. The equations derived from the above values are given in Table II.

TABLE I

MOLAR EXTINCTION COEFFICIENTS OF THE COBALT, NICKEL AND COPPER COMPLEXES

	385 mμ	*440 mμ*	*640 mμ*
ε_{Co}	12,950	12,500	618
ε_{Ni}	4,360	3,920	8,930
ε_{Cu}	15,800	6,060	4,010

Recommended procedure. The optimum conditions for the determination of cobalt, nickel and copper are those under which the absorbances of the complexes are the greatest, the most stable and the most reproducible. The results described up to this point show that these conditions are fulfilled by measuring the absorbance of a solution at 440 mμ, 640 mμ, and 385 mμ, against a reagent blank containing 2 ml reagent solution, which has been prepared as follows: the complexes are formed at a pH of 9.0 ± 0.3 in the presence of 4 ml of a 0.1% gum acacia solution by adding 3 ml of a $1.5 \cdot 10^{-3} M$ reagent solution. Dilute to 25 ml, mix and measure the absorbances at the indicated wavelengths. The molar concentrations of the ions are then calculated by using the spectrophotometric equations listed in Table II.

Interference of cobalt upon the determination of nickel. When solutions containing cobalt, nickel and copper were analysed by the above procedure, it was found that in some cases only one-half to one-third of the nickel added was recovered. This incomplete recovery was not encountered when samples containing only nickel and copper were analysed. However, when the complexes were developed individually and

TABLE II

SPECTROPHOTOMETRIC EQUATIONS USED

One of three ions present

$$(\mathrm{Co}) \cdot 10^5 = 8.00\ A_{s440}$$
$$(\mathrm{Ni}) \cdot 10^5 = 11.2\ A_{s640}$$
$$(\mathrm{Cu}) \cdot 10^5 = 6.17\ A_{s385}$$

Two of three ions present

$$(\mathrm{Cu}) \cdot 10^5 = 10.4\ A_{s385} - 10.8\ A_{s440}$$
$$(\mathrm{Co}) \cdot 10^5 = 13.2\ A_{s440} - 5.06\ A_{s385}$$

$$(\mathrm{Cu}) \cdot 10^5 = 7.23\ A_{s385} - 3.53\ A_{s640}$$
$$(\mathrm{Ni}) \cdot 10^5 = 12.8\ A_{s640} - 3.24\ A_{s385}$$

$$(\mathrm{Co}) \cdot 10^5 = 8.17\ A_{s440} - 3.58\ A_{s640}$$
$$(\mathrm{Ni}) \cdot 10^5 = 11.4\ A_{s640} - 0.57\ A_{s440}$$

Three ions present

$$(\mathrm{Co}) \cdot 10^5 = 12.1\ A_{s440} - 3.76\ A_{s385} - 3.46\ A_{s640}$$
$$(\mathrm{Ni}) \cdot 10^5 = 11.6\ A_{s640} - 4.08\ A_{s440} - 4.50\ A_{s385}$$
$$(\mathrm{Cu}) \cdot 10^5 = 10.8\ A_{s385} - 11.0\ A_{s440} - 0.30\ A_{s640}$$

then mixed before making measurements, the results were good. This phenomenon suggested that when the nickel complex was formed in the presence of cobalt, there was a shift in the absorbance peak of the nickel complex. It was further observed visually that when the concentration of nickel to cobalt was large (*ca.* 4 to 8) the effect appeared to be less pronounced. In order to determine this ratio precisely, the following experiment was performed: solutions were prepared which contained 0.40 p.p.m. cobalt and concentrations of nickel varying from 1.00 p.p.m. to 4.00 p.p.m. A blank was used which contained 0.40 p.p.m. cobalt. Since the absorbance due to the cobalt complex was subtracted in each case by the blank, the absorbances observed at each wavelength were those of the nickel complex. The results of this experiment are shown in Fig. 7. When the ratio of nickel to cobalt is 7 or greater, there is no shift in the nickel complex absorbance peak.

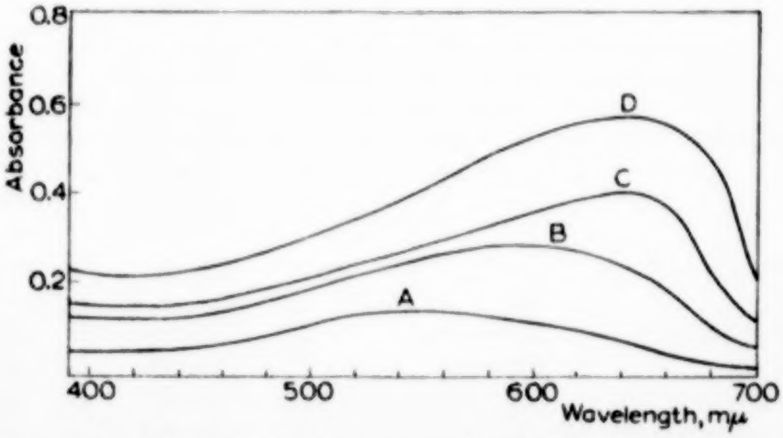

Fig. 7. Effect of 0.40 p.p.m. cobalt on (A) 1.00 p.p.m. nickel, (B) 2.00 p.p.m. nickel, (C) 3.00 p.p.m. nickel and (D) 4.00 p.p.m. nickel.

Analysis of synthetic samples and NBS standard samples

A series of synthetic samples and three National Bureau of Standards samples were analyzed by the procedure finally adopted. Each sample had the indicated ion concentration, 4 ml of a 0.1% gum acacia solution, 3 drops of a 0.1% thymolphthalein solution and was adjusted to a pH 9.0 ± 0.3 with ammonium hydroxide and hydrochloric acid until the blue color of the indicator just turned colorless. Three ml of a $1.5 \cdot 10^{-3} M$ reagent solution was added. The samples were diluted to the mark in 25

TABLE III

ANALYSIS OF SYNTHETIC SAMPLES

Sample	*Added (p.p.m.)*	*Found (p.p.m.)*
1	Ni 0.40	0.39
	Cu 2.40	2.47
2	Co 0.80	0.69
	Cu 2.00	2.06
3	Ni 1.00	1.14
	Cu 2.00	2.06
4	Co 0.40	0.44
	Ni 3.00	3.07
	Cu 2.00	1.85
5	Co 0.40	0.39
	Ni 3.50	3.66
	Cu 1.50	1.30
6	Co 0.40	0.31
	Ni 4.00	4.07
	Cu 1.00	0.98

TABLE IV

ANALYSIS OF NATIONAL BUREAU OF STANDARDS SAMPLES

Material	*NBS Value %*		*Found*	
			% Ni	*% Cu*
Al alloy	Ni 0.41			
85a	Cu 2.48		0.42	2.42
			0.33	2.52
			0.39	2.38
			0.41	2.47
		av.	0.39	2.45
Al–Si alloy	Ni 0.59		0.54	0.28
87	Cu 0.30		0.58	0.30
			0.58	0.31
			0.60	0.30
		av.	0.58	0.30
Ferro-silicon	Ni 0.115		0.100	0.039
alloy 58	Cu 0.04		0.106	0.031
			0.107	0.032
			0.107	0.037
		av.	0.105	0.035

ml volumetric flasks, mixed and the absorbances measured at the respective wavelengths against a reagent blank which contained 2 ml of reagent solution. The results are given in Tables III and IV.

In order to prevent the precipitation of the hydrated oxides of aluminum and iron when the NBS samples 85a, 87 and 58 were analysed, the aluminum was complexed with 5 ml of a 5% sodium fluoride solution in the case of aluminum alloys 85a and 87 and the iron in the ferro-silicon alloy, 58, was extracted by diethyl ether from a 20% hydrochloric acid solution.

SUMMARY

The cobalt, nickel and copper complexes of dithio-oxamide have been characterized in terms of color, effect of pH, structure *in solution*, order of addition of reagents, adherence to Beer's law and sensitivity. The reactivity of the reagent to other ions has been reported.

A method for the simultaneous spectrophotometric determination of cobalt, nickel and copper has been developed. The results of the application of this procedure to synthetic samples and to several National Bureau of Standards Samples are given.

RÉSUMÉ

Les complexes du cobalt, du nickel et du cuivre avec la dithioxamide ont été examinés. Une méthode spectrophotométrique de dosages simultanés de ces trois éléments est proposée.

ZUSAMMENFASSUNG

Es werden die Komplexe von Kobalt, Nickel und Kupfer mit Dithiooxamid beschrieben und über eine spektrophotometrische Methode zur gleichzeitigen Bestimmung dieser drei Elemente berichtet.

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DETERMINATION OF MICROGRAM AMOUNTS OF COBALT IN SODIUM METAL*

2-NITROSO-1-NAPHTHOL SPECTROPHOTOMETRIC METHOD

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The valuable properties of pure sodium as coolant in certain types of atomic energy reactors are well known. After a calculated long-term operational period, the reactor must be shut down and the fuel rods exchanged. During the operational period the sodium and its impurities are subjected to irradiation and a "cooling" or "decay" period is foreseen at the shutdown. One of the many possible elements present in the sodium which could enforce an unusually long cooling period is cobalt, because of the likely presence of a long-lived cobalt isotope. Calculations show that not more than 2 p.p.m. of cobalt are permissible in the sodium, in order to prevent an uneconomically long cooling period before the irradiated sodium can be safely transported and handled.

Several colorimetric methods for analyzing small amounts of cobalt were examined. The reagent, 2-nitroso-1-naphthol, appeared to be the most applicable and it is this reagent which is used. A technique similar to that employed by ALMOND[1] for determining cobalt in soils was developed. The cobalt forms a complex with the reagent at a pH of 4 to 8.5. Other impurities such as ferric iron, copper and nickel cause no interference since the ferric iron does not complex at this pH and the copper and nickel complexes present in small amounts, are removed by washing.

APPARATUS AND REAGENTS

Apparatus

Spectrophotometer. Beckman spectrophotometer, Model DU, supplied with 5-cm cells.

pH Meter. Beckman pH meter, Model H was used.

Separatory funnels. Ultramax type with teflon valves to contain the carbon tetrachloride. 250-ml and 125-ml capacities.

Reagents

Reagent solution. Prepare 0.01% solution of 2-nitroso-1-naphthol by adding 2 drops of 1*N* sodium hydroxide and a small amount of water to 0.01 g of 2-nitroso-1-naphthol. Stir until in solution and dilute to a 100-ml volume.

Standard cobalt solutions. Dissolve 4.954 g of $Co(NO_3)_2 \cdot 6H_2O$ in H_2O and dilute to 1 l. Fume 100 ml with 1 ml H_2SO_4 and dilute to 1 l. Make subsequent dilutions from the sulfate solution. Standardize by direct ignition or by the 1-nitroso-2-naphthol gravimetric method.

Borate buffer[1]. Dissolve 19 g of $Na_2B_4O_7 \cdot 10H_2O$ in 800 ml of H_2O, add 10 ml of concentrated NH_4OH, and dilute to 1 l.

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* This report is based on studies conducted for the Atomic Energy Commission under Contract AT-11-1-GEN-8.

EXPERIMENTAL RESULTS

Effect of chloride

Preliminary studies were made using 25 g of sodium chloride, dissolved in 100 ml of water, to simulate a 10-g sample of sodium metal converted to the chloride. It was quickly noted that 6 μg of cobalt could not be extracted from an aqueous solution of low chloride content. In a 100-ml volume, it is requisite to have a minimum of 3 g of sodium chloride for complete cobalt recovery (Fig. 1).

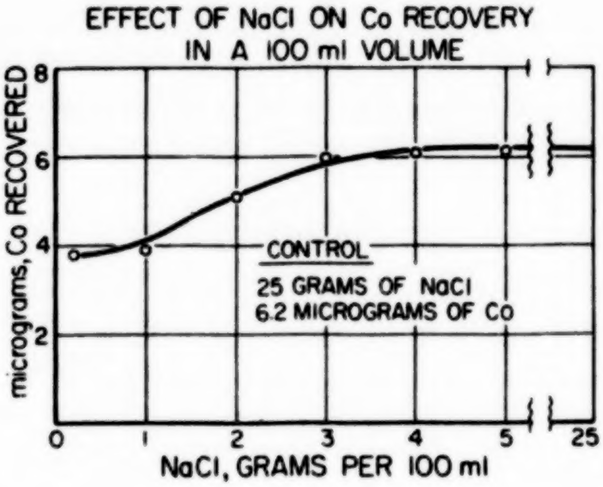

Fig. 1.

Removal of excess reagent

A brief study showed that 5 ml of the reagent (0.01%) was optimum, for the conditions used. The excess reagent present can be effectively removed by shaking the carbon tetrachloride extract with 4% sodium hydroxide containing a few drops of 10% potassium cyanide. This is shown by a low absorbance reading at 410 mμ, characteristic for this reagent.

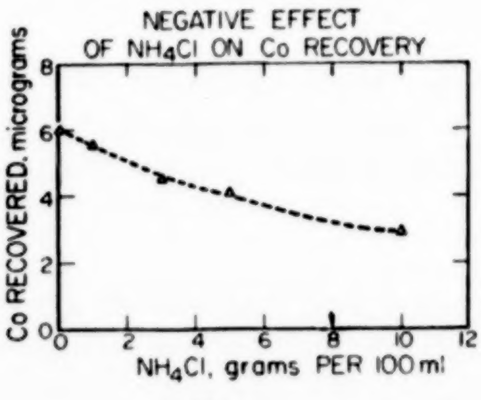

Fig. 2.

Effect of alkali metal ions

Potassium, lithium and sodium ions have no effect on the formation of the cobalt complex.

Ammonium ions of the order of gram quantities have an adverse effect on the formation of the cobalt complex with the 2-nitroso-1-naphthol (Fig. 2) despite the favorable presence of sodium chloride.

References p. 343

Effect of other metal ions

The amounts of the various foreign metals in commercial sodium metal are such that no interference occurs.

Ferric iron does not form a complex with the reagent at the 6.5 pH used; citrate is added to prevent hydrolytic precipitation of the iron.

The copper and nickel form complexes with the reagent but are removed in the same step which removes the excess reagent. Should larger amounts than normally present in sodium metal of these two ions exist, their removal can be effected by an additional washing step, in which the complexes in the carbon tetrachloride are shaken with hydrochloric acid[2]. Proportionally larger amounts of the reagent, 2-nitroso-1-naphthol are also required, so that these ions can be completely complexed and thus prevent possible incomplete formation of the cobalt complex.

PROCEDURE

Quickly weigh a portion (about 10 g) of the sodium metal to be analyzed and transfer the sodium metal into a Vycor test tube. Maintain a rapid flow of nitrogen over the surface of the sodium. Add water dropwise to the sodium, allowing time for the reaction to subside between additions. After the metal has completely reacted, wash the sodium hydroxide into a 250-ml beaker and then neutralize with hydrochloric acid. Add 1 ml of 10% ammonium citrate to the resulting salt solution and adjust the pH to 6.5 with borate buffer. Transfer the solution to a 250-ml separatory funnel, and add 5 ml of 0.01% 2-nitroso-1-naphthol. Extract the colored complexes by shaking 3 min with exactly 20 ml of carbon tetrachloride. Drain the carbon tetrachloride layer into a 125-ml separatory funnel which contains 10 ml of a 4% sodium hydroxide solution and 1 drop of 10% potassium cyanide solution. Shake for 15 sec. This step removes interfering complexes and excess reagent. Shake the carbon tetrachloride layer with 10 ml of 1% sodium chloride to remove small amounts of sodium hydroxide which might damage spectrophotometer cells. Filter the carbon tetrachloride through cotton into a small flask. Carry a reagent blank through the procedure.

Transfer the sample and the blank to 5.0-cm cells and measure the absorbance using carbon tetrachloride as reference at 535 mμ. Correct the sample for the blank reading and obtain the amount of cobalt present from the standard curve.

Standard curve

Prepare a series of samples containing known amounts of cobalt (0 to 10 μg) Adjust the volume to 100 ml, and add 25 g of sodium chloride (to simulate a 10-g sample of sodium). These are carried through the same procedure as given for the analysis of the sodium starting with the addition of 1 ml of 10% ammonium citrate. Correct the absorbances obtained for reagent blank, and plot on linear graph paper *versus* the μg of cobalt. A straight line is obtained. (The molar absorption coefficient is 11,780.)

DISCUSSION

Several reagents for determining μg amounts of cobalt were studied. Of these, the most favorable were tetraphenylarsonium chloride–thiocyanate, diethyldithiocarbamate and 2-nitroso-1-naphthol. The determination of cobalt as tetraphenylarsonium cobaltothiocyanate was not sufficiently sensitive, having a working range of approximately 20 to 100 μg when a range of 1 to 10 μg was desired for determining cobalt in sodium. The molar absorption coefficient for this reagent was found to be 1,800.

Diethyldithiocarbamate had been used by CHILTON[3,4] whereby copper, nickel, and cobalt were determined simultaneously. This reagent was quite sensitive for cobalt, having a molar absorption coefficient of 14,000. However, attempts to apply this method to determining cobalt in sodium were unsuccessful.

2-Nitroso-1-naphthol is also a very sensitive reagent for determining cobalt. The molar absorption coefficient was found to be 11,780.

Using 2-nitroso-1-naphthol as the reagent for determining cobalt, μg amounts of cobalt could be successfully extracted from 25 g of sodium chloride dissolved in 100 ml of water.

When experimentally extracting the small amounts of cobalt from a 100-ml volume of water, it was found necessary to have a minimum of 3 g of sodium chloride present (Fig. 1). The sodium chloride apparently furnishes the requisite chloride ion to complete extraction of the cobalt.

Using a 10-g sample of sodium, 0.1 p.p.m. of cobalt can be determined. The optical density for 1 μg of cobalt in 20 ml of carbon tetrachloride, corrected for a reagent blank, is 0.05 when measured in a 5-cm spectrophotometer cell. The standard deviation was found to be 5% of the value.

SUMMARY

A colorimetric method, with 2-nitroso-1-naphthol, is outlined for determining cobalt in sodium metal, which is used as a coolant in nuclear reactors. The sodium metal is reacted with water, neutralized with hydrochloric acid, and the cobalt content determined; the cobalt nitrosonaphtholate is extracted with carbon tetrachloride and the absorbance is measured at 535 mμ. Chloride ion is requisite for the extraction of the cobalt complex in dilute solutions. Lithium and potassium as well as sodium have no effect. Ammonium ions have an adverse effect. As little as 0.1 p.p.m. cobalt can be determined in sodium metal. In order to determine cobalt in the fractional p.p.m. range, 10 g of sample are used. The molar extinction coefficient is 11,780.

RÉSUMÉ

Une méthode colorimétrique est proposée pour le dosage du cabalt dans le sodium métallique, utilisé dans les réacteurs nucléaires. Le nitrosonaphtolate de cobalt est extrait au moyen de tétrachlorure de carbone. On mesure l'absorption à 535 mμ.

ZUSAMMENFASSUNG

Es wird eine colorimetrische Methode zur Bestimmung von Kobalt in Natrium-Metall, das als Kühlmittel in Kern-Reaktoren verwendet wird, beschrieben. Das Kobalt wird als Kobalt-nitrosonaphtholat mit Tetrachlorkohlenstoff extrahiert und die Absorption der Lösung bei 535 mμ gemessen.

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THE COULOMETRIC DETERMINATION OF SULFUR IN SILICON-IRON

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INTRODUCTION

Within the last few years there has been an increasing demand for a better method for the control analysis of sulfur in ferrous materials (especially silicon-iron) where the sulfur content is in the range of 0.0001 to 0.002 % by weight.

There are three methods that may be used for routine control purposes[1] given below:

(1) *Gravimetric method.* Conversion of sulfur to sulfate, precipitation as barium sulfate.

(2) *Evolution of sulfur as H_2S*, absorbing as an insoluble sulfide in an alkaline solution, followed by titrating with iodine in an acid solution.

(3) *Combustion method.* Burning the material in oxygen and (a) absorbing the oxides of the sulfur followed by titration with a standard alkaline solution, (b) absorbing the oxide sulfur gases into an acid iodine–iodide solution held at a constant iodine concentration by titrating with a standard iodate solution.

The first two methods are obviously unsatisfactory; the gravimetric procedure is time-consuming and unsuitable for such low percentages of sulfur, and the evolution technique is limited to materials containing no constituents that form acid-insoluble sulfides. Consequently, the combustion process (although empirical) has become predominant for routine sulfur analysis. Commercial apparatus is available for rapid sulfur analysis by the combustion technique. However, the minimum amount of sulfur that can be determined is 0.001% with a reproducible precision of ± 0.001%. Nevertheless, the rapidity of the combustion process in converting the sulfur in metals to SO_2 indicated that a method for the determination of smaller amounts of sulfur should be a refinement of existing technique rather than an entirely new attack upon the problem. The method described in this report is an adaption of the conventional combustion process to a coulometric titration technique sensitive enough to determine sulfur at the 0.0001% level.

CHEMISTRY

Two methods of determining the amount of sulfur (as SO_2) obtained by the combustion of the sample were used with equal success. In both cases, the number of coulombs of electricity necessary to oxidize sulfite ion to sulfate ion was an exact measure of the SO_2 obtained by the combustion process. Both methods are outlined below.

Direct method

The gases from the combustion tube were passed through distilled water to absorb the SO_2 as H_2SO_3[2]. This solution was added to an acid KBr solution containing a small amount of KI in a specially constructed cell with provisions for the generation of Br_2 (and I_2)[3] by electrolysis at constant current. The reactions in the cell are the following:

(a) At the generator anode:

$$2Br^- = Br_2 + 2e \qquad (1)$$

$$2I^- = I_2 + 2e \qquad (2)$$

(b) In the solution:

$$Br_2 + 2I^- = I_2 + 2Br^- \qquad (1)$$

$$SO_3^{-2} + H_2O + I_2 = SO_4^{-2} + 2I^- + 2H^+ \qquad (2)$$

There also may be the reaction:

$$SO_3^{-2} + H_2O + Br_2 = SO_4^{-2} + 2Br^- + 2H^+ \qquad (3)$$

but the large amount of KI relative to the SO_3^{-2} concentration makes this improbable. In order to determine when the oxidation of SO_3^{-2} to SO_4^{-2} was complete, the cell contained two indicator electrodes, with a potential impressed across them such that a very small current flow was obtained, the reactions being:

In the absence of I_2

$$2H^+ + 2e = H_2 \text{ (cathode)}$$

$$2I^- = I_2 + 2e \text{ (anode)}$$

The reaction at the indicator cathode becomes

$$I_2 + 2e = 2I^-$$

with the first excess of I_2. This results in a large increase in the indicator current which indicates the completion of the titration.

Indirect method

In this case the gases from the combustion furnace were passed through an aqueous solution of potassium ferricyanide, the sulfite apparently being oxidized to sulfate with the corresponding reduction of ferricyanide to ferrocyanide. This solution was titrated in the same cell by electrolytically generated Br_2. The end-point was determined by the increase in the indicator current at the first excess of Br_2. The reactions taking place are:

$$2Br^- \rightarrow Br_2 + 2e \text{ (generator anode)} \qquad (1)$$

$$Br_2 + 2Fe(CN)_6^{-4} \rightarrow 2Br^- + 2Fe(CN)_6^{-3} \text{ (in soln.)} \qquad (2)$$

$$2Br^- \rightarrow Br_2 + 2e \text{ (indicator anode)} \qquad (3)$$

$$2H^+ + 2e \rightarrow H_2 \text{ (indicator cathode before excess } Br_2\text{)} \qquad (4)$$

$$Br_2 + 2e = 2Br^- \text{ (with excess } Br_2\text{)} \qquad (5)$$

EXPERIMENTAL EQUIPMENT

The combustion unit was a commercial induction model manufactured for use in routine sulfur analysis of iron and steel. The O_2 purifying train preceding the combustion unit was set up exactly as specified by the manufacturer. Fig. 1 is a schematic illustration of the gas absorption vessel and titration cell and Fig. 2 is a photograph of this assembly. The gases from the combustion furnace were passed into the absorption cell in the same manner as they were passed into a conventional titration cell.

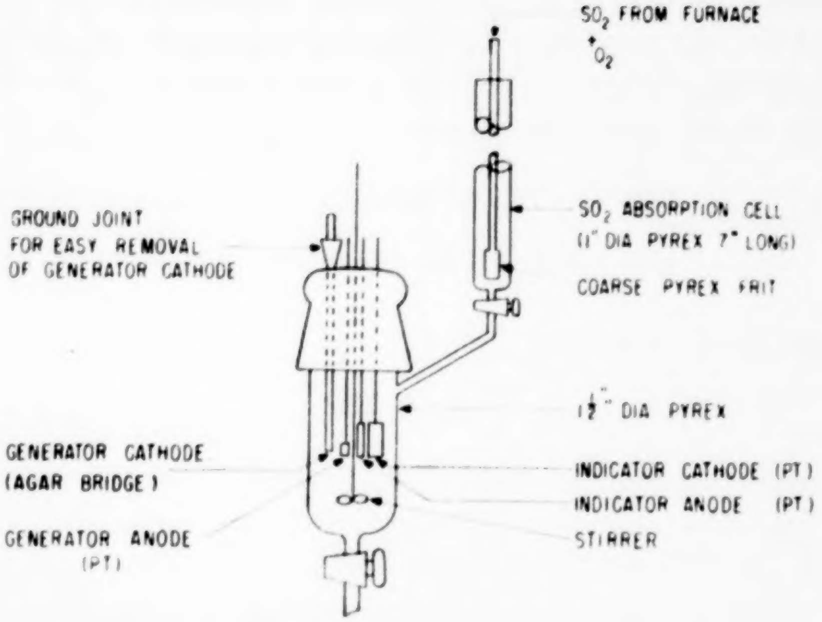
SO2 FROM FURNACE
+O2
GROUND JOINT
FOR EASY REMOVAL
OF GENERATOR CATHODE
SO2 ABSORPTION CELL
(1" DIA PYREX 7" LONG)
COARSE PYREX FRIT
1½" DIA PYREX
GENERATOR CATHODE
(AGAR BRIDGE)
INDICATOR CATHODE (PT)
INDICATOR ANODE (PT)
GENERATOR ANODE
(PT)
STIRRER

Fig. 1. Schematic illustration of low sulfur titration cell.

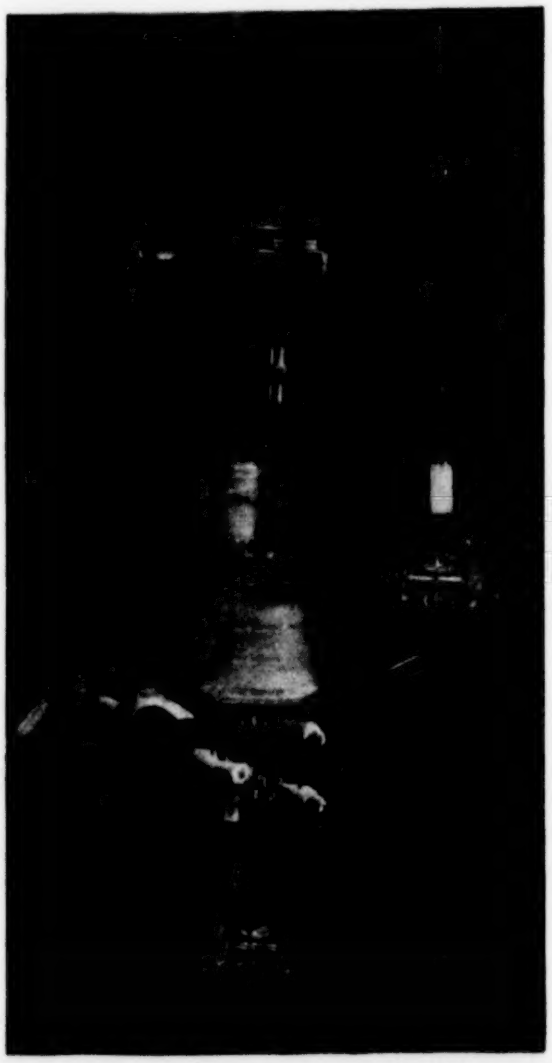

Fig. 2. The absorption and titration cell.

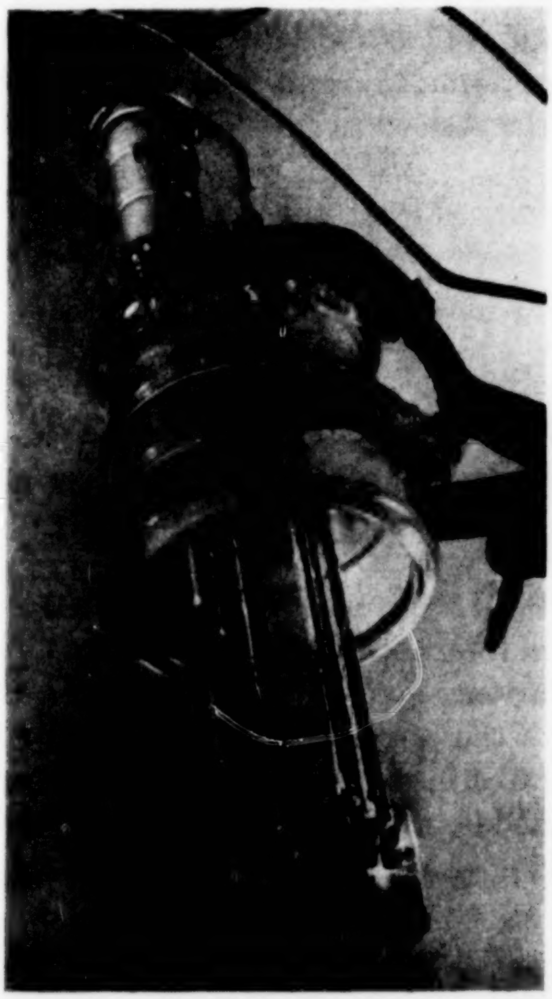

Fig. 3. The generator and indicator electrodes

The generator anode and both indicator electrodes were made of platinum sheet, spot-welded to platinum wire sealed into pyrex tubing. The relative positions of the electrodes are shown in Fig. 3.

The absorption cell and titration cell were fitted with suitable side arms (shown in Fig. 2) so that all the necessary solutions for collecting gases, titrating, and rinsing

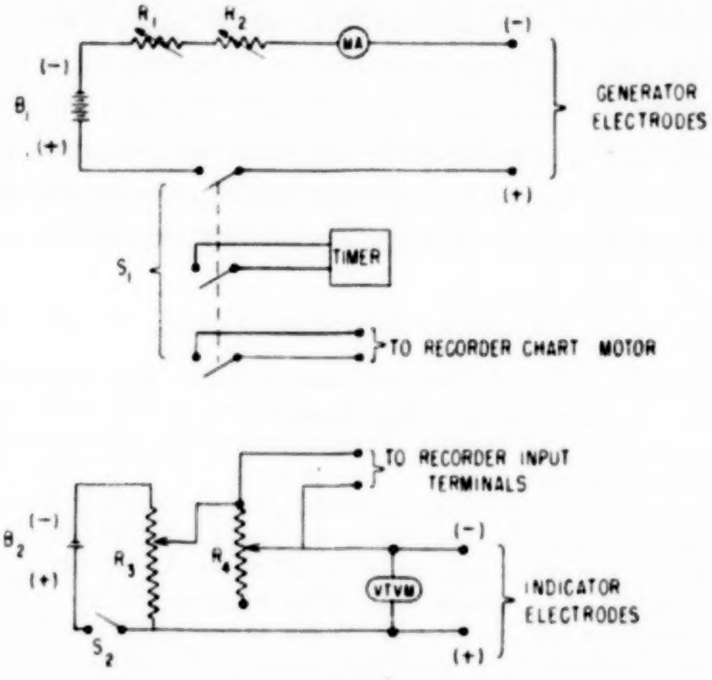
R1
R2
MA
(−)
(−)
B1
(+)
GENERATOR ELECTRODES
(+)
S1
TIMER
TO RECORDER CHART MOTOR
TO RECORDER INPUT TERMINALS
(−)
B2
(+)
R3
R4
VTVM
(−)
INDICATOR ELECTRODES
(+)
S2

Fig. 4. Wiring diagram.

B_1: 45 V, dry cell; B_2: 1.5 V, dry cell; R_1: 2000 KΩ variable; R_2: 20 KΩ variable; R_3: 100 Ω variable; R_4: 2 KΩ variable; MA: 0.05 to 100 mA, d.c., multiple range; VTVM: vacuum tube volt meter, 1.2 V; S_1: 3 SPST switches, ganged to operate together; S_2: SPST switch; Timer: accurate to 0.01 minute; Recorder: 10 mV, L & N speedomax.

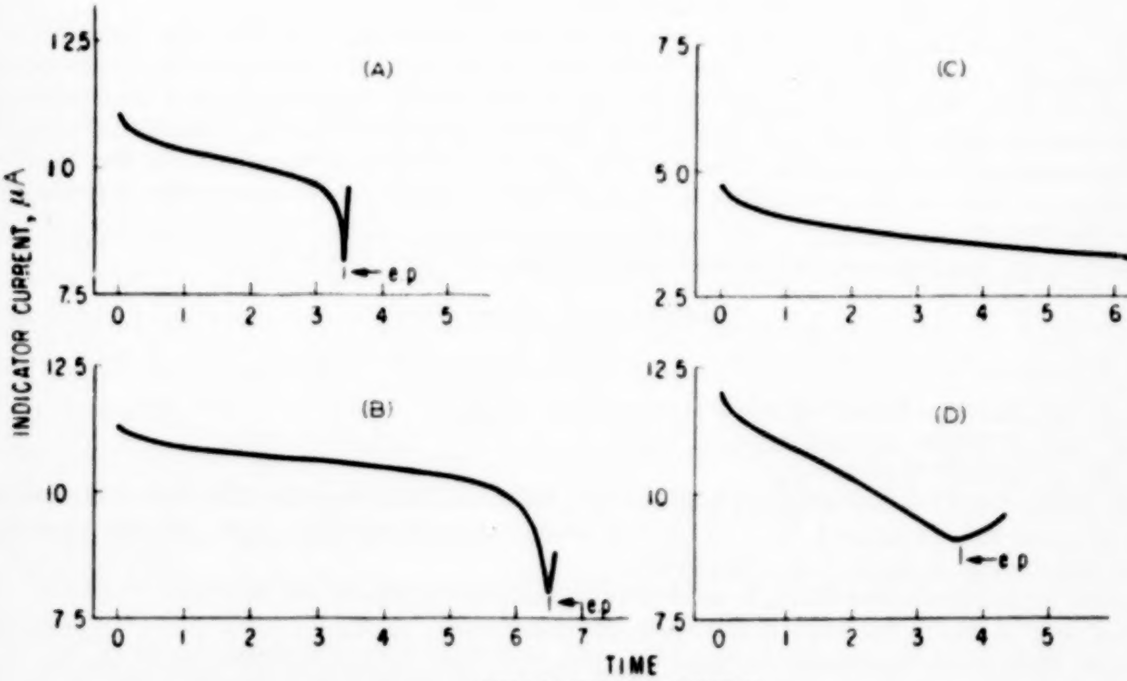

Fig. 5. Indicator current *vs.* time curves showing end-point sensitivity as a function of generator current; (A) Sample No. 8, Table II, 5 mA, gen. current; (B) Sample No. 3, Table IV, 2 mA, gen. current; (C) Sample No. 4, Table IV, 2 mA, gen. current; (D) Sample No. 16, Table III, 0.2 mA, gen. current.

could be admitted from reservoir bottles, controlled by means of air pressure. The KBr acid solution and the KI solutions were dispensed from automatic leveling burets. The titrating cell was constructed to hold 125 ml of solution with the stirrer operating. The absorption cell was constructed to hold 20 ml of solution with the O_2 flow set at 0.5 to 1 liter per minute.

The power supply and wiring is shown in Fig. 4. By using a 45-V dry cell as a current source for the generator electrodes, the stability of the circuit was more than adequate to obtain results in the range of precision desired. The indicator current was recorded by a Leeds and Northrup "Speedomax" 10 mV potentiometer recorder (Fig. 5). However, the chart speed of the instrument was not constant enough to use it to determine the time required for each titration. An electric timer, accurate to 0.01 min connected in the generator circuit was necessary for this data.

EXPERIMENTAL PROCEDURE

The experimental manipulation of burning the sample, collecting the SO_3 from the combustion process and titrating the collected sample was carried out in the same manner for all the materials investigated, except where differences were intentionally introduced in order to investigate the obvious variables of the method.

The oxygen flow rate was held at 0.8 l/min. 1 g of reagent-grade tin was used as a flux throughout the investigation. All samples were burned for a minimum of 5 min and a maximum of 7 min. The volume of gas-collecting solution was 20 ml in all cases. Loose fitting crucible lids, supplied by a manufacturer of crucibles for carbon and sulfur analyses, were employed. These lids were pre-fired by burning a charge of low-sulfur iron in the same manner as the experimental samples were burned. Unlike the crucibles, they were not severely damaged during the combustion process and could be used several times before it was necessary to discard them.

The generator current was adjusted to the desired value prior to running a series of determinations by filling the cell with the same solution that was used in the actual titrations, and adjusting the variable resistors R_1 and R_2. It was not necessary to change these resistance settings for subsequent determinations at the same generator current.

Immediately following combustion the absorption solution was drained into the titration cell (Fig. 1), which contained 80 ml of the acid solution containing KBr and/or KI, the stirrer turned on, and the titration carried out without unnecessary delay.

In order to facilitate rapid titration of the sample after collecting the SO_3, the recorder was turned on during the combustion period, the timer was set at zero, the indicator electrode potential was set at 0.2 V by means of R_4 (see Fig. 4) and S_2 was closed. Therefore, after the collecting solution was drained into the cell and the stirrer started, closing switch S_1 began the titration and simultaneously started the recorder chart and timer. The total time necessary for the titration was obtained by observing the recording of the indicator current and manually stopping the timer at the end-point.

The calculation of the per cent sulfur was made using the equation below:

$$\%S = \frac{(0.09618 \cdot 10^{-3})\ (i)\ (t)\ (100)}{W}$$

where: i = generator current in mA,
t = titration time in min,
W = sample weight in g.

The figure $0.09618 \cdot 10^{-3}$ is the weight (in g) of the sulfur contained in the SO_3^{-2} that is oxidized to SO_4^{-2} when one mA is passed for 1 min, calculated from Faraday's Law (96,500 coulombs necessary to oxidize, or reduce, 1 g-equivalent).

Experiments were conducted using four different sample materials, as follows;

(a) H-6435, a 3-1/4% Si-Fe alloy containing less than 0.001 % S.
(b) National Bureau of Standards Sample No. 36a, a Cr-Mo steel containing 0.018 % S.
(c) National Bureau of Standards Sample No. 132a, a Mo-W steel containing 0.006 % S.
(d) National Bureau of Standards Sample No. 125a, a 3.32% Si-Fe containing 0.013 % S.

The majority of the experiments were conducted using an aqueous solution containing 1 g/l of potassium ferricyanide to absorb the SO_3. The absorption solution was drained into a solution that was $2M$ in HCl and $0.1M$ in KBr.

A few experiments were conducted using distilled water to absorb the SO_3. In order to obtain a good end-point it was necessary to add 5 ml of an iodide solution (20 mg KI/l H_2O) to the HCl–KBr solution before titrating.

Crucibles obtained from two manufacturers were used, designated as type "A" and type "B" in this report. Type "A" is a mullite ceramic, and Type "B" a zirconia ceramic. Both types are manufactured for routine sulfur and carbon analysis by combustion methods. Experiments were conducted using each type in the "as-received" condition and after a pre-ignition firing in air at 1550° for 16 h.

In addition, titrations at different generator currents were made on two materials as well as variations in the sample weights to investigate the effect of these variables on the results obtained.

RESULTS AND CONCLUSIONS

Tables I through IV contain results of the experiments described. The letters R or I following the crucible type designation indicate the crucibles were used in the "as-received" condition or the pre-ignited condition respectively. Except for 3 samples (indicated in Table IV) the gas absorbent was the ferricyanide solution already described.

TABLE I

NBS STANDARD NO. 132a[a]

(Mo-W Steel)

Sample No.	*Sample wt. (grams)*	*Crucible type*	*Generator current (milliamps)*	*% Sulfur found*
1	1.000	A-R	2.0	0.0037
2	1.500	A-I	2.0	0.0038
3	1.500	A-R	2.0	0.0040
4	1.000	A-I	2.0	0.0033
5	1.000	A-R	2.0	0.0034
6	1.000	A-I	2.0	0.0035
7	1.500	A-I	2.0	0.0038
8	1.000	B-I	2.0	0.0044
9	1.000	B-R	2.0	0.0056
10	1.250	B-I	2.0	0.0059
11	1.250	B-R	2.0	0.0060

[a] NBS average value 0.006 % S.

The results tabulated in Table I show the difference in results obtained using both crucible types on a standard material containing less than 0.01 % S but greater than 0.001 % S. Comparison of the results of samples 1 through 7 with samples 8–11 indicate that the zirconia crucibles contain an impurity that results in an error of between 0.001 and 0.002 % S. Prefiring does not affect the results appreciably. Table I also indicates that the sample size taken for analysis can be varied from 1.0 g to 1.5 g without introducing significant error.

Table II is a tabulation of results obtained with a standard sample containing 0.018 % S (by conventional combustion methods). The average value for sulfur for all thirteen determinations (no results were discarded) is 0.017 %. The standard deviation is 0.001 %. The results indicate that the coulometric titration method could be used for materials containing up to 0.02 % S, although the method shows no advantages over the conventional combustion techniques presently employed for the determination of sulfur contents of this magnitude. The zirconia crucibles were used

TABLE II

NBS STANDARD NO. 36a[a]

(Cr-Mo Steel)

Sample No.	*Sample wt. (grams)*	*Crucible type*	*Generator current (milliamps)*	*% Sulfur found*
1	1.000	B-R	5.0	0.0159
2	1.000	B-R	5.0	0.0174
3	1.000	B-R	5.0	0.0184
4	1.000	B-R	10.0	0.0187
5	1.000	B-R	5.0	0.0159
6	1.000	B-R	5.0	0.0163
7	1.000	B-R	5.0	0.0160
8	1.000	B-R	5.0	0.0175
9	1.000	B-R	5.0	0.0163
10	1.000	B-R	10.0	0.0191
11	1.000	B-R	5.0	0.0166
12	1.000	B-R	5.0	0.0167
13	1.000	B-R	5.0	0.0184

[a] NBS average value 0.018 % S.

TABLE III

3.25 % SILICON IRON (LOW SULFUR)

Sample No.	*Sample wt. (grams)*	*Crucible type*	*Generator current (milliamps)*	*% Sulfur found*
1	1.000	A-R	0.5	0.00030
2	1.000	A-R	0.5	0.00040
3	1.000	A-R	1.0	0.00055
4	1.000	A-R	0.5	0.00065
5	1.500	A-R	0.5	0.00040
6	1.500	A-R	0.5	0.00033
7	1.000	A-I	0.5	0.00023
8	1.000	A-I	0.5	0.00033
9	1.500	A-I	0.5	0.00030
10	1.500	A-I	0.5	0.00036
11	1.500	A-I	0.2	0.00025
12	1.500	A-I	0.2	0.00015
13	1.500	A-I	0.2	0.00020
14	1.500	A-I	0.2	0.00013
15	1.500	A-I	0.2	0.00057
16	1.500	A-I	0.2	0.00048
17	1.500	A-I	0.2	0.00029
18	1.500	A-I	0.2	0.00033
19	1.500	A-I	0.2	0.00039
20	1.000	B-I	0.5	0.0023
21	1.000	B-I	0.5	0.0018
22	1.500	B-I	0.5	0.0020

for these samples because it was felt that the error caused by impurities was not large enough to be significant, and also because the supply of "Mullite" crucibles was limited and, therefore, reserved for the critical experiments on low sulfur silicon-iron samples.

Table III is a compilation of results using a silicon–iron alloy with a sulfur content below 0.001 %. Samples Nos. 1–19 were run using the "Mullite" crucibles, both in the "as-received" and the "pre-fired" condition. During the course of determining the sulfur content of these 19 samples, the generator current was varied from 0.2 mA to 1.0 mA, and the sample weights varied from 1.0 g to 1.5 g. Changes in sample weight, generator current, or prior treatment of the crucibles had no significant effect upon the amount of sulfur found. On the other hand, examination of the results of samples Nos. 20–22 shows that the zirconia crucibles, even after extended pre-firing are unsuitable for use for the determination of sulfur at this level and support the conclusions drawn after experiments using NBS Standard No. 132a (Table I).

The average value for sulfur, using the results of samples Nos. 1–19, discarding no results, is 0.00035 %. The standard deviation (σ), for all 19 determinations is 0.00014 % and the 3σ value is 0.00042 %.

Table IV shows the results of experiments using distilled water in place of the ferricyanide solution to absorb the gas from the combustion unit and indicates that this is a satisfactory technique, for low sulfur contents, as discussed above. However, the necessity of adding KI to the HCl–KBr solution in the titration cell, in order to obtain a sharp end-point makes the ferricyanide absorbing solution seem more convenient in actual practice.

TABLE IV[a]

Sample No.	*Sample material*	*Sample wt. (grams)*	*Crucible type*	*Generator current (milliamps)*	*% Sulfur found*
1	3.25 % Si-Fe	1.500	A-R	0.2	0.00040
2	3.25 % Si-Fe	1.500	A-R	0.2	0.00027
3	NBS No. 125a	1.500	A-R	2.0	0.0088
4	NBS No. 125a	1.500	A-R	2.0	0.0087

[a] Samples Nos. 1, 2 and 4: SO_2 collected in water, and end-point detected by indicator current due to excess I_2. Sample No. 3 run in same manner as those in Table I.

ACKNOWLEDGEMENTS

The authors would like to thank R. E. FRYXELL, of the Transformer Laboratories Department, General Electric Company, who supplied the low-sulfur silicon-iron and the mullite crucibles, and R. L. FULLMAN of the Research Laboratory Staff for assistance in the preparation of the manuscript.

SUMMARY

A coulometric method for the determination of sulfur in metallurgical products has been developed which meets the needs of production control of low sulfur contents. The method is rapid and more precise than the conventional combustion technique.

References p. 352

RÉSUMÉ

Une méthode coulométrique, rapide et précise, est proposée pour le dosage du soufre dans les produits métallurgiques.

ZUSAMMENFASSUNG

Es wird eine schnelle und genaue coulometrische Methode zur Bestimmung von Schwefel in metallurgischen Produkten beschrieben.

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A QUICK AND PRECISE HETEROMETRIC MICRODETERMINATION OF TRACES OF PALLADIUM IN METALS WITH NITRON

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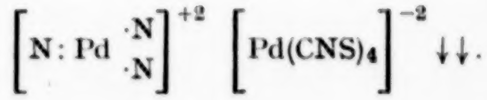
INTRODUCTION

The reaction of palladium (II) with nitron in the presence of *large excesses of thiocyanate* has been studied previously[1]. In this investigation it was our intention to examine the reaction from the analytical point of view and to see if traces of palladium could be determined in *the presence of large excesses of foreign metals.* All the usual masking agents were tried out. It was very interesting to establish that the presence of very large excesses of trisodium citrate, disodium tartrate, pyro-, tripolyphosphate and disodium-EDTA had no influence on the results of the determination of palladium. The reaction, in the absence of bi- and polyvalent cations, proceeded with the same success at all pH values between 1–8. In most cases the amount of palladium present was less than 0.5%. In spite of this a complete titration took only 5–10 min, and the error found was generally between 0 and 1%. The *specificity* of the reaction is demonstrated by the fact that, amongst all the bi-, tri- and polyvalent metals, *palladium* is the *only* metal (with the exception of gold(III)) that gives an insoluble compound in the presence of the masking agents used. In all cases when nitron was used as titrant, only one compound, $Pd_2N_3 \downarrow\downarrow$ (N = nitron) was obtained quantitatively at the end-point. The structures of the complexes of palladium, gold and platinum with nitron in thiocyanate solutions have been discussed elsewhere[1]. It was shown that this compound may be best presented as a salt, composed of cation and anion complexes



$$\left[N:Pd\begin{matrix}\cdot N\\ \cdot N\end{matrix}\right]^{+2}\left[Pd(CNS)_4\right]^{-2}\downarrow\downarrow.$$

EXPERIMENTAL

The same instrument and the same working conditions were used as in previous heterometric investigations[2]. The fundamental principles of heterometry have been presented before[3].

Reagents

All the chemicals used were either Baker AnalaR or chemically pure reagents.

Nitron (mol. wt. = 312.16). 0.7802 g nitron (Eastman Organic Chemicals, for chemical purposes) + 7 ml *M* CH_3COOH were dissolved in water and made up to 250 ml, giving a 0.01 *M* solution. More dilute solutions were prepared from the standard solution. All solutions were kept in dark brown bottles. The dilute solutions were freshly prepared every few days.

Palladium chloride (Johnson Matthey). 1 g $PdCl_2$ + 56 ml *M* HCl were dissolved in water to give a volume of 562.8 ml (= 0.01 *M*). More dilute solutions were prepared from the standard solution.

METHOD

General

20 ml aqueous solution containing $\sim$0.5 mg palladium and 2 ml *M* potassium thiocyanate and which may contain 99.5% of polyvalent cations, in addition to masking agents, are titrated heterometrically with 0.0015*M* – 0.002*M* nitron.

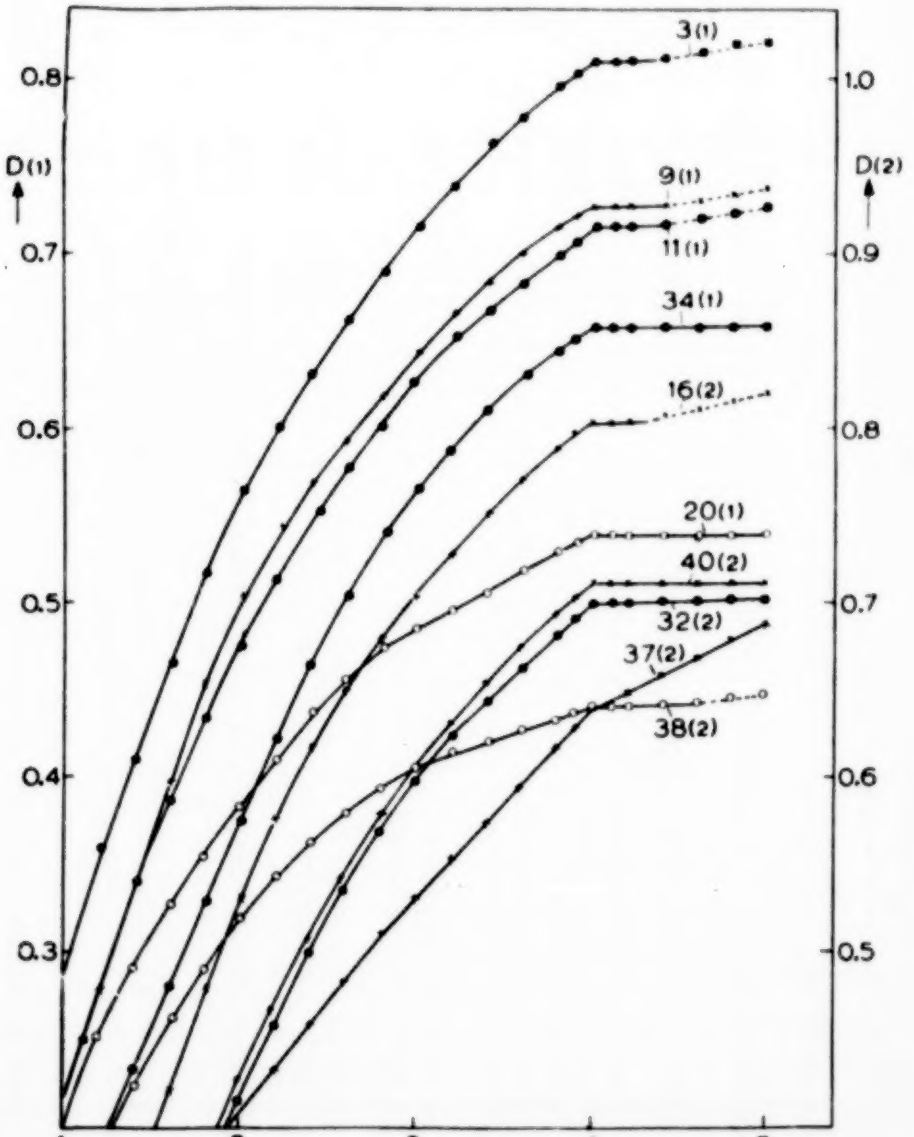


Fig. 1. Titrations of palladium chloride with nitron.

TABLE I

General composition: 4 ml 0.001M $PdCl_2$ + 2 ml M KCNS + a ml supplements + H_2O ad 20 ml + x ml 0.0015M nitron.
Temp. = 20°; content palladium = 0.4268 mg.

Expt. No.	*Supplements*	*% Pd*	*ml nitron at the end-point*	*Maximum density value*	*ml nitron at initial ppt.*	*% error*	*Titration time in min*	*Remarks*
1	3 ml M HCl		i 3.98 h	0.66	0.2	0.5	8	Beige ppt.
2	3 ml M CH_3COOH		i 4.00 h	0.67	0.2	0.0	7	Beige ppt.
3	1 ml M H_3PO_4		i 4.00 h	0.81	0.2	0.0	9	Beige ppt.
4	1 ml M CH_3COONa		i 4.00 h	0.78	0.2	0.0	7	Beige ppt.
5	2 ml 0.5M Na_2HPO_4		i 4.0 sh.h	0.74	0.2	0.0	7	Beige ppt.
6	8 ml 0.125M $Na_5P_3O_{10}$		i 4.02 sh.h	0.65	0.2	0.5	8	Beige ppt.
7	8 ml 0.125M $Na_4P_2O_7$		i 4.00 sh.h	0.67	0.2	0.0	12	Beige ppt.
8	4 ml M NH_4NO_3		i 4.00 h	0.60	0.4	0.0	5	Beige ppt.
9	3 ml M Na_3-citrate		i 3.99 h	0.73	0.2	0.3	7	Beige ppt.
10	3 ml M Na_2-tartrate		i 4.00 h	0.73	0.2	0.0	5	
11	10 ml 0.2M Na_2-EDTA		i 4.0 sh.h	0.72	0.2	0.0	6	Beige ppt.
12	3 ml 0.2M Na_4-EDTA			0.0	>5			
13	1 ml M NH_3			0.0	>5			Colourless solution
14	10 ml ethanol			0.0	>5			Yellow solution
15	2 ml 0.5M Na_2HPO_4 + 1 ml 0.2M KCN			0.0	>5			Colourless solution
16	2 ml 0.5M Na_2HPO_4 + 3 ml M Na_3-citrate		i 4.0 sh.h	0.80	0.2	0.0	9	Beige ppt.
17	1 ml M CH_3COONa + 2 ml M KF		i 4.00 h	0.70	0.2	0.0	8	Beige ppt.
18	2 ml M $Ca(NO_3)_2$	0.53	i 4.00 h	0.54	0.4	0.0	7	Beige ppt.
19	5 ml M Na_3-citrate + 4 ml M $Ca(NO_3)_2$	0.27	i 4.00 h	0.72	0.4	0.0	7	Beige ppt.; slight linear increase after the end-point
20	1 ml M $BaCl_2$	0.31	i 3.98 h	0.54	0.4	0.5	6	Beige ppt.
21	5 ml M Na_3-citrate + 2 ml M $BaCl_2$	0.15	i 3.98 h	0.76	0.4	0.5	6	Beige ppt.
22	2 ml M $MgCl_2$	0.87	i 3.97 h	0.54	0.4	0.8	7	Beige ppt.
23	5 ml M Na_3-citrate + 4 ml M $MgCl_2$	0.43	i 4.0 sh.h	0.79	0.2	0.0	8	Beige ppt.
24	3 ml M Na_3-citrate + 2 ml M $ZnSO_4$	0.33	i 4.0 sh.h	0.76	0.2	0.0	7	Beige ppt.
25	4 ml M Na_3-citrate + 3 ml M $MnCl_2$	0.26	i 4.00 h	0.75	0.2	0.0	7	Beige ppt.

i = intersection point; h = horizontal maximum density line; sh.h = short horizontal; in = increase.

TABLE I (Continued)

Expt. No.	*Supplements*	*% Pd*	*ml nitron at the end-point*	*Maximum density value*	*ml nitron at initial ppt.*	*% error*	*Titration time in min*	*Remarks*
26	1 ml *M* $Al(NO_3)_3$	1.6	i 4.00 h	0.71	0.6	0.0	7	Beige ppt.
27	4 ml *M* Na_3-citrate + 2 ml *M* $FeCl_3$	0.38	i 4.0 sh.h	0.76	0.2	0.0	8	Beige ppt.
28	3 ml *M* Na_3-citrate + 2 ml *M* $Cr(NO_3)_3$	0.41	i 3.98 sh.h	0.43	0.4	0.5	9	The colour of the solution is intense green-blue
29	3 ml *M* Na_3-citrate + 2 ml *M* $Co(NO_3)_2$	0.36	i 4.00 h	0.73	0.2	0.0	7	Carmine solution
30	5 ml *M* Na_3-citrate + 4 ml *M* $Ni(NO_3)_2$	0.18	i 4.00 h	0.74	0.2	0.0	7	Beige ppt.
31	10 ml 0.2*M* Na_2-EDTA + 2 ml 0.2*M* $UO_2(NO_3)_2$	0.45	i 4.00 h	0.67	0.2	0.0	5	Yellow solution; regular ppt.
32	3 ml *M* Na_3-citrate + 5 ml 0.2*M* $UO_2(NO_3)_2$	0.18	i 4.00 h	0.70	0.2	0.0	6	Beige ppt.
33	3 ml *M* Na_3-citrate + 2 ml 0.4*M* $SbCl_3$	0.44	i 4.01 h	0.65	0.4	0.3	7	Beige ppt.
34	3 ml *M* Na_3-citrate + 0.5 ml *M* $Bi(NO_3)_3$	0.41	i 4.00 h	0.66	0.2	0.0	7	Beige ppt.
35	8 ml 0.125*M* $Na_5P_3O_{10}$ + 0.5 ml *M* $Cd(NO_3)_2$	0.38	i 4.02 sh.h	0.76	0.2	0.5	6	Beige ppt.
36	8 ml 0.125*M* $Na_5P_3O_{10}$ + 5 ml 0.1*M* $Pb(NO_3)_2$	0.41	i 3.99 h	0.71	0.4	0.3	7	Beige ppt.
37	3 ml *M* Na_3-citrate + 2 ml 0.2*M* $Hg(NO_3)_2$	0.53	i 4.00	0.64	0.2	0.0	7	Beige ppt; linear increase after the end-point
38	3 ml *M* Na_3-citrate + 2 ml *M* $CuSO_4$	0.34	i 4.00 h(in)	0.54	0.2	0.0	8	Beige ppt.
39	8 ml 0.125*M* $Na_5P_3O_{10}$ + 5 ml 0.1*M* $TlNO_3$	0.42	i 4.0 sh.h	0.72	0.2	0.0	10	Beige ppt.
40	3 ml *M* Na_3-citrate + 5 ml 0.1*M* $Th(NO_3)_4$	0.37	i 4.00	0.71	0.4	0.0	7	
41	3 ml *M* Na_3-citrate + 1 ml 0.2*M* $ZrO(NO_3)_2$	2.3	i 4.0 sh.h	0.75	0.4	0.0	11	Beige ppt.
42	3 ml *M* Na_3-citrate + 5 ml 0.2*M* $Ce(NO_3)_3$	0.30	i 4.0 sh.h	0.76	0.2	0.0	5	Beige ppt.

i = intersection point; h = horizontal maximum density line; sh.h = short horizontal; in = increase.

Remarks

1. In the absence of polyvalent cations the titration may be carried out at pH's 1–8 with or without masking agents.

2. 3 to 5 ml *M* Na_3-citrate must be added if the following cations are present: Ca^{+2}, Ba^{+2}, Mg^{+2}, Mn^{+2}, Zn^{+2}, Co^{+2}, Ni^{+2}, UO_2^{+2}, Fe^{+3}, Cr^{+3}, Al^{+3}, Sb^{+3}, Bi^{+3}, Hg^{+2}, Cu^{+2}, Th^{+4}, Ce^{+3} and ZrO^{+2}.

3. Solid $Na_5P_3O_{10}$ (or $K_5P_3O_{10}$) as powder (equal to $\sim$ 1 ml *M* solution) must be added when Cd^{+2}, Pb^{+2} or Tl^{+} are present.

4. The nitrate content of the solution being analysed may be as high as 8 ml *N* NO_3^-.

RESULTS

Table I shows the compositions and the results of a selection of heterometric titrations, which were carried out with the purpose of studying the sensitivity and the precision of the determination of palladium in the presence of various supplements including polyvalent metal salts. Contracted courses of a few titrations are given in Fig. 1. (The same numeration is used in the table and in the figure). The amount of the foreign metal present, as cited in the table, was generally approximately equal to the maximum amount that could be present without causing interferences in the results. In some cases (Expts. 18, 20 and 22) the maximum density value was much lower than usual although the usual end-point was still obtained. When these titrations were carried out in the presence of excesses of sodium citrate, normal maximum density values were obtained. The detrimental effect of the foreign metal was not observed then, although this metal content was doubled (compare Expts. 19, 21 and 23). Generally the maximum density value showed only small fluctuations in the experiments. This indicates that the variation in the pH between pH$\sim$1 and pH$\sim$9, as well as the presence of large amounts of cations, had no influence on the reaction measured (Expts. 1–11). In the presence of Na_4-EDTA, KCN or NH_3 — even when the last mentioned was dilute — the reaction studied did not take place (Expts. 12–15). Only a few foreign cations could be present without the necessity of using masking agents at all. They were: Ca^{+2}, Ba^{+2} and Mg^{+2}. Under our working conditions the solution being analysed could contain as much as 4 ml *M* NH_4NO_3 without interferences being observed (Expt. 8). In individual cases the nitrate content was even doubled! (Expt. 30).

The various masking agents used and their amounts in the individual cases can be seen in Table I. We found that an excess of trisodium citrate (at pH$\sim$7) was more successful than other complexing agents in the presence of the following cations: Ca^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Co^{+2}, Ni^{+2}, Fe^{+3}, Cr^{+3}, Al^{+3}, UO_2^{+2}, Sb^{+3}, Bi^{+3}, Cu^{+2}, Hg^{+2}, Th^{+4}, Ce^{+3}, and $(ZrO)^{+2}$. In all cases the molar ratio of [citrate] : [cation] was higher than 1 : 1. Yet, even in the presence of citrate only restricted amounts of Al^{+3} could be present without harm.

By doubling the amount of Al^{+3} low density values were obtained and the end-points were no longer clear. In the presence of $(UO_2)^{+2}$, both Na_2-EDTA and Na_3-citrate could be used successfully as masking agents, but citrate is to be preferred since greater amounts of uranium could be masked (Expts. 31 and 32). In the presence of Cd^{+2}, Pb^{+2} and Tl^{+} tripolyphosphate must be used (Expts. 35, 36 and 39).

SUMMARY

A heterometric study was made of the reaction between palladium chloride and nitron in thiocyanate solutions in the presence of excesses of various masking agents.

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A method is presented for the heterometric determination of ~0.5 mg palladium in 20 ml aqueous solution with nitron, which can be carried out within 5–10 min. The solution to be analysed may in general contain ~99.5% of the following foreign metals as cations: Ca^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Co^{+2}, Ni^{+2}, Al^{+3}, Fe^{+3}, Cr^{+3}, UO_2^{+2}, Cu^{+2}, Cd^{+2}, Hg^{+2}, Pb^{+2}, Tl^{+}, Sb^{+3}, Bi^{+3}, Th^{+4}, Ce^{+3} and ZrO^{+2}.

The error is between 0 and 1%.

RÉSUMÉ

Les auteurs ont effectué une étude hétérométrique de la réaction entre le palladium et le nitron, en solution thiocyanique et en présence de divers réactifs de masquage en excès. Une méthode de dosage est proposée.

ZUSAMMENFASSUNG

Es wurde eine heterometrische Untersuchung der Reaktion zwischen Palladiumchlorid und Nitron in thiocyanathaltiger Lösung und in Gegenwart eines Überschusses verschiedener Maskierungsmittel durchgeführt; eine Bestimmungsmethode für Palladium wird beschrieben.

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SOLUBILIZATION CHROMATOGRAPHY

III. ETHERS, CARBOXYLIC ACIDS, AND HYDROCARBONS

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In previous papers of this series, solubilization chromatography was applied to the separation of alcohols[1], phenols[1], and ketones[2]; and the general principles of the method were discussed. In the present paper, probably the last of the series, solubilization chromatography is applied to ethers, fatty acids, and hydrocarbons; also some experiments with a special resin of low capacity are described which throw further light on the nature of attraction between the resin and the organic solutes.

EXPERIMENTAL

Materials

All ethers, acids, and hydrocarbons used in this study were of the best grade commercially available. No further purification was required.

The resins used in these studies included: the strong-acid cation exchanger, Dowex-50; the strong-base anion exchanger, Dowex-1; the resinous adsorbent with a phenolic matrix and mixed polar functional groups, Duolite S-30; the "snake-cage" resin made from Dowex-1 and acrylic acid, Retardion 11A8[3]; polystyrene crosslinked with divinylbenzene; and a Dowex-50 resin of approximately one-half normal capacity.

The ratio of the interstitial volume to the bed volume; V/V_B, was determined for several of the resins used[4], and found to be: 0.333 for Dowex-50-X4, Lot No. 4177-40; 0.402 for Dowex-1-X4, Lot No. 1241; 0.371 for Dowex-50W-X8, Lot No. L·3937-40, capacity (Q) = 1.99 meq/g.

Eluents were prepared by dilution of reagent-grade glacial acetic acid and absolute ethanol.

Elutions

The samples were introduced onto the resin bed as previously reported[5]. The flow rate of eluent was 0.4 to 0.5 cm/min, unless otherwise specified. Fractions of approximately 5.0 ml were automatically collected with the aid of a constant-volume collecting device[6].

Analysis

Fractions containing acetic acid were analyzed by mixing them with 5.0 ml of 0.02M sodium dichromate in concentrated sulfuric acid, diluting with 25 ml of distilled water, and measuring spectrophotometrically the resultant Cr(III)[7]. All the solutes studied in this paper reduce dichromate.

Since the substituted benzenes and naphthalenes studied absorb light in the ultraviolet (225 to 289 mμ) region[8], the ethanolic eluates of these solutes were analyzed by ultraviolet absorption spectroscopy.

RESULTS AND DISCUSSION

Elution variables

Since the effects of such elution variables as choice of resin, particle size of resin, flow rate of eluent, sample size, etc. have been clearly established for both salting-out[5] and solubilization chromatography[1], no further study of these variables was made.

Dowex-50-X4 and Dowex-1-X4 were the resins primarily used. The low percentage of crosslinking was used to permit rapid diffusion of the large molecules encountered in this investigation.

One ml of feed solution was used in each elution. The solution contained 0.20 mmole of solute in an aqueous solution of the organic constituent of the eluent, concentrated enough to cause complete dissolution. Small volumes of feed solutions more concentrated in the organic constituent than the eluent itself were shown to cause insignificant change in the position of the elution maxima[1].

Acetic acid was chosen as the eluent for the ethers and acids because the spectrophotometric determination of the chromic ion produced by the reduction of dichromate is the most convenient method available for the determination of small amounts of these compounds in effluent fractions; and acetic acid is one of the few organic compounds not oxidized by dichromate. Ethanol was employed as an eluent for the hydrocarbons.

With each series of solutes studied, the elution variables just mentioned were kept constant at their optimum values while the most important variable, the concentration of the eluent solution, was varied. Values of the distribution ratio, C, were calculated by the equation[6]

$$U^* = CV + V \qquad (1)$$

where U^* is the volume of effluent collected from the point of addition of the sample to the peak of the elution graph and C is the distribution ratio of the solute (the total quantity of compound in the resin of any plate divided by the quantity in the solution of the same plate). The interstitial volume of the column is represented by V.

Ethers

Table I shows the distribution ratios, as calculated by equation (1), for the ethers

TABLE I

ELUTION DATA OF ETHERS ON DOWEX-50-X4, HYDROGEN FORM, 200-400 MESH

[HAc]	*0.0*	*1.0*	*2.0*	*4.0*	*6.0*	*Negative slope of plot of log C vs. M*	*Extent of linearity of plot of log C vs. M*
Diisopropyl ether	3.51	3.11	2.88	2.13	1.30	0.043	0–2M
Di-*n*-propyl ether	4.94	4.16	3.37	2.08	1.65	0.083	0–6M
Ethyl *n*-butyl ether	5.25	4.19	3.60	2.48	1.69	0.083	0–6M
Di-*n*-butyl ether	12.5	9.36	6.81	3.90	1.83	0.127	0–4M
Anisole	15.2	11.6	9.09	5.36	3.08	0.116	0–6M
Diphenyl ether	—	—	54.6	19.2	6.65	0.226	2–6M
Diisoamyl ether	—	—	—	—	2.28	—	—
Di-*n*-amyl ether	—	—	—	—	3.03	—	—

with eluents 0 to 6M in acetic acid and the results obtained by plotting log C *vs.* M. These results indicate the following:

1. Because of their greater solubility in aqueous solvents, branched-chain compounds are eluted before (have lower distribution ratios than) their straight-chain isomers.

2. The elution behavior of di-*n*-propyl ether and ethyl *n*-butyl ether is very similar, as is to be expected from their similar solubility characteristics.

3. Contrary to the results of salting-out chromatography[5], but similar to the previously published results of solubilization chromatography[1,2], some of the plots of log C *vs.* M are linear for only a limited region. At large molarities of acetic acid, the graphs tend to curve downward and converge. These results indicate that the change in solubility with molarity of acetic acid for these solutes is probably also nonlinear. This was shown to be true for two alcohols[1].

4. Similar to the earlier results of salting-out chromatography[5] and solubilization chromatography[1,2], the slopes of these plots (solubilization constants) are seen to increase as the ethers become less soluble in aqueous solutions.

5. Values of the distribution ratios of diisoamyl and di-*n*-amyl ethers, for eluents less concentrated than 6M acetic acid, could not be determined because of unsatisfactory elution graphs. With 4M acetic acid, both ethers gave elution graphs which rose to peaks immediately after the effluent volume equalled the interstitial volume, and then tailed for a large volume of effluent. This is probably due to the fact that most of these very large ether molecules are excluded from the resin by virtue of their size and eluted right after the interstitial volume. The molecules which do diffuse inside the resin are trapped there and cause the considerable tailing. Similar behavior was exhibited by di-*n*-hexyl ether in 6M acetic acid.

When introduced onto the resin bed with 6M, 4M and 2M acetic acid eluents, diphenyl ether was precipitated as a white solid on the brown column of Dowex-50.

The precipitate redissolved and the band disappeared as the elution took place. The first two eluents gave completely satisfactory elution graphs; the latter yielded a very flat, severely spread peak. These results are probably due to the rates of redissolving in the various eluents used.

The elution data in Table I were used to plan[6,9] the separation of a synthetic mixture of 0.20 mmole of each of five ethers (Fig. 1). The calculated positions for the ether peaks and the actual U^* values were within experimental error. Di-*n*-propyl ether could have been included in the separation instead of ethyl *n*-butyl ether, but under the given elution conditions, it would have overlapped the peak of diisopropyl ether.

The elution behavior of diisoamyl ether, di-*n*-amyl ether, and di-*n*-hexyl ether was studied on Dowex-50-X2, Duolite S-30, and Retardion 11A8 in an attempt to get elution data which could be used to effect the separation of these compounds. None of these resins gave satisfactory results with eluents of a useful concentration range. It would have been possible to get symmetrical elution graphs for these compounds by use of extremely concentrated solutions of acetic acid. However, with these eluents the resin would show no selectivity among the three solutes. In effecting separations by solubilization chromatography, it is always necessary to find an eluent–resin combination which gives good selectivity and elution peaks which are both symmetrical and narrow. As is seen here, this is not always possible.

Carboxylic acids

Aqueous acetic acid and Dowex-50-X4, hydrogen form, were chosen for the study of the solubilization chromatography of the naturally occurring fatty acids. This system obviated any ion-exchange reactions between the acids and the resin phase.

Fig. 2 shows the separation of approximately 0.20 mmole of each of five acids and the plots of log *C* *vs.* *M* from which the conditions for the separation were chosen. Table II contains a summary of the elution data shown in the figure.

It is seen that with the acids, plots of log *C* *vs.* *M* of acetic acid are linear over the entire concentration range studied. There seems to be no way of predicting linearity or nonlinearity for a given compound.

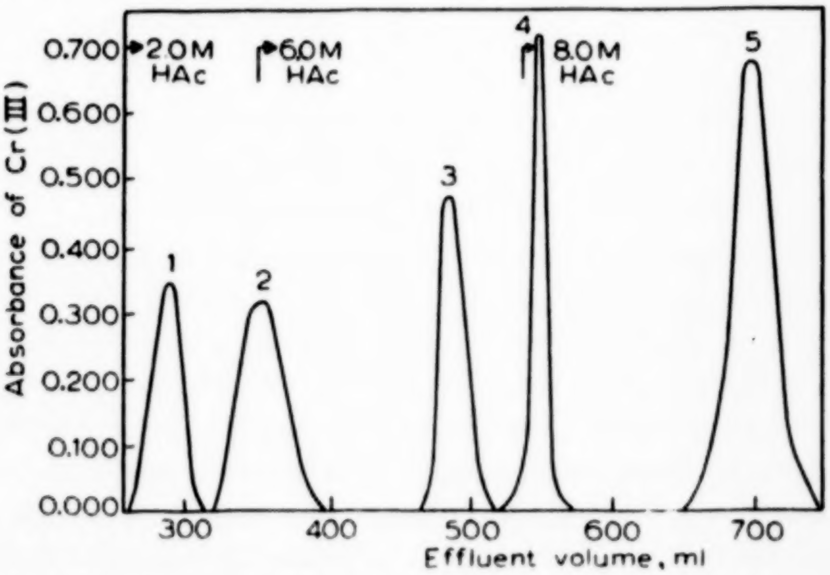

Fig. 1. The separation of a five-component ether mixture. 102.0 cm × 2.28 cm² Dowex-50-X4, 200–400 mesh, hydrogen form, 0.28 cm/min. Aqueous acetic acid eluent changed at 350 ml and 550 ml. 1. diisopropyl ether; 2. ethyl *n*-butyl ether; 3. di-*n*-butyl ether; 4. anisole; 5. diphenyl ether.

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TABLE II

ELUTION DATA OF ACIDS ON DOWEX-50-X4, HYDROGEN FORM, 200-400 MESH

	C				Negative slope of plot of log C vs. M	Extent of linearity of plot of log C vs. M
[HAc]	0.0	2.0	4.0	6.0		
Butyric acid	2.17	1.81	1.45	1.24	0.041	0-6M
n-Caproic acid	4.99	3.35	2.01	1.40	0.092	0-6M
n-Caprylic acid	18.0	7.74	3.29	1.43	0.184	0-6M
n-Capric acid	—[a]	24.4	6.22	1.63	0.294	2-6M

[a] Too large to be accurately determined.

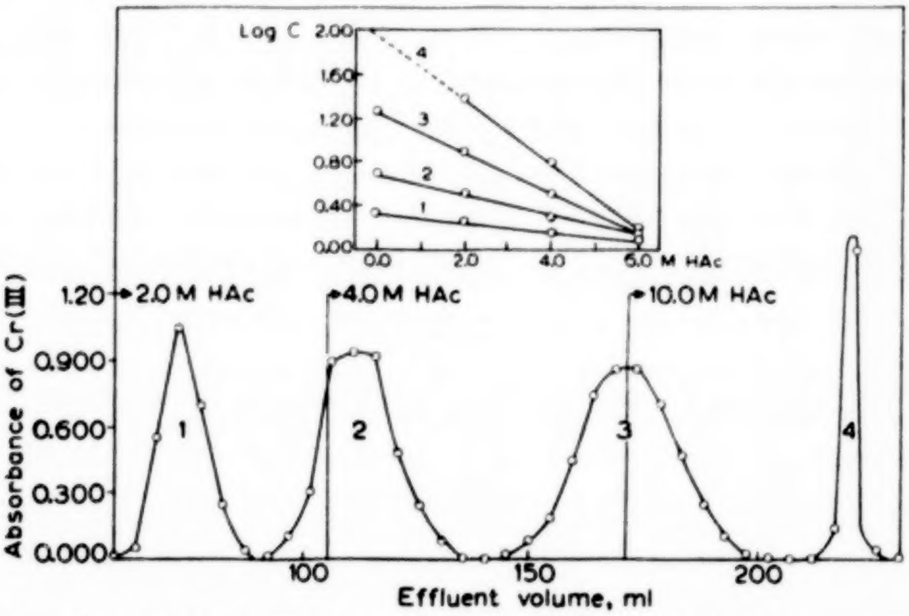

Fig. 2. Plots of log *C vs. M* for four acids and the separation of a four-component acid mixture planned from these data. 19.0 cm × 3.90 cm² Dowex-50-X4, 200-400 mesh, hydrogen form, 0.28 cm/min. Aqueous acetic acid changed at 105 ml and 170 ml. 1. butyric acid; 2. *n*-caproic acid; 3. *n*-caprylic acid; 4. *n*-capric acid.

From the length of the column used, it is obvious that this series was the easiest to separate of those studied in this and past work. This is because the constituents differed from each other by two carbon atoms, and had correspondingly large differences in their relative solubilities in aqueous solutions of acetic acid.

The twelve-carbon member, lauric acid, was precipitated when introduced onto a bed of resin equilibrated with even 6*M* acid. Some of the compound then appeared in the effluent immediately after the interstitial volume, but most of it was irreversibly sorbed and did not move from the top of the bed even after a large volume of effluent had passed. For this reason the study was stopped with *n*-capric acid.

Hydrocarbons

Because of the partially successful application of reversed-phase partition chromatography to the separation of methyl-substituted benzenes and naphthalenes with aqueous solutions of ethanol as the mobile phase, these eluents were initially tried in an attempt to improve these separations by use of solubilization chromatography.

However, solutions as concentrated as 50% ethanol by volume proved unsuccessful with Dowex-1-X4, Dowex-50-X4, and crosslinked polystyrene as the solid phase. In each case, severe tailing of the elution graphs occurred.

Acetic acid proved a satisfactory eluent for these hydrocarbons in that symmetrical elutions were in general obtained with Dowex-1 and Dowex-50. The use of crosslinked polystyrene again resulted in elution graphs with severe spread. This is due to the fact that polystyrene does not swell in aqueous solutions of acetic acid and adsorption rather than true absorption is the factor controlling equilibrium. Tailing is characteristic of adsorption phenomena. There is no obvious explanation why acetic acid should prove a much superior eluent than ethanol for the hydrocarbons when they were shown[2] to effect ketone elutions in a very similar manner.

A study was made of the effect of concentration of acetic acid on the elution behavior of these various benzene and naphthalene derivatives. Table III shows the results for Dowex-50-X4 and Dowex-1-X4 in terms of values of *C*. These data show, as was found for the alcohols[1], that Dowex-1 is a much stronger absorbent for organic solutes than is Dowex-50 because of its more hydrocarbon nature.

Toluene was visibly precipitated on the column equilibrated with 1.0*M* acetic acid and the elution graph spread severely. The same results were found for *m*-xylene with 2.0*M* acetic acid, mesitylene with 4.0*M* acetic acid, and durene with 6.0*M* acetic acid.

TABLE III

ELUTION DATA OF HYDROCARBONS ON DOWEX-50-X4, HYDROGEN FORM, AND DOWEX-1-X4, ACETATE FORM, 200-400 MESH

	Dowex-50-X4 *C*					*Dowex-1-X4* *C*	
[*HAc*]	*1.0*	*2.0*	*4.0*	*6.0*	*8.0*	*6.0*	*8.0*
Benzene	6.62	5.69	4.21	2.69		4.55	
Toluene	10.2	8.21	5.36	3.00		5.53	
m-Xylene		14.2	7.76	3.75		7.41	
Mesitylene			13.0	5.12		9.66	
Naphthalene					2.92	15.8	7.48
β-Methylnaphthalene					3.37	22.4	9.40
1,4-Dimethylnaphthalene					4.21	30.2	11.0

The plots of log *C* *vs.* *M* for the benzenes on Dowex-50-X4 begin to curve downward and converge at 4.0*M* acetic acid.

The elution data of Table III were sufficient to calculate[5,8] the conditions for the separation of 0.20 mmole of each of the seven solutes studied. Fig. 3 shows the conditions used and results obtained for this separation. The calculated positions of the peaks were 305, 359, 462, 542, 774, 860 and 952 ml, as compared with actual U^* values of 294, 354, 464, 549, 770, 869, and 956 ml.

The final two components were not completely separated by use of the given conditions because of the severe spread of the elution peaks. A complete separation of these two peaks could not be accomplished on a convenient-sized column of Dowex-1-X4.

Dowex-1-X4 was chosen in preference to Dowex-50-X4 for this separation because of the greater selectivity exhibited by the former resin for the compounds studied. An elution similar to that shown in Fig. 3 would require a column of Dowex-50-X4 well in excess of 100 cm.

Low-capacity resins

To test the usefulness of low-capacity resins in solubilization chromatography, several alcohols were eluted with acetic acid from a Dowex-50-X8 resin of less than one-half normal exchange capacity. Table IV compares the results of these elutions with those for the same alcohols on a Dowex-50-X8 resin of usual capacity and similar column dimension.

It is seen that although the low-capacity resin exhibits great selectivity among the three solutes studied, the severe spread of the elution peaks more than offsets this beneficial effect. It appears that resins of low capacity are useless for the chromatography of organic compounds of high molecular weight.

Theory of the process

Solubilization chromatography is a partition chromatography on ion-exchange resins. It differs from usual partition chromatography in that the two "phases" between which the solute is partitioned consist of the same solvent, and interactions between the "solid support" and the solute are important. Such interactions include (1) ion-dipole attractions of the functional group of the resin and/or its counter ion for the solute, and (2) London dispersion forces between the solute and the hydrocarbon part of the resin.

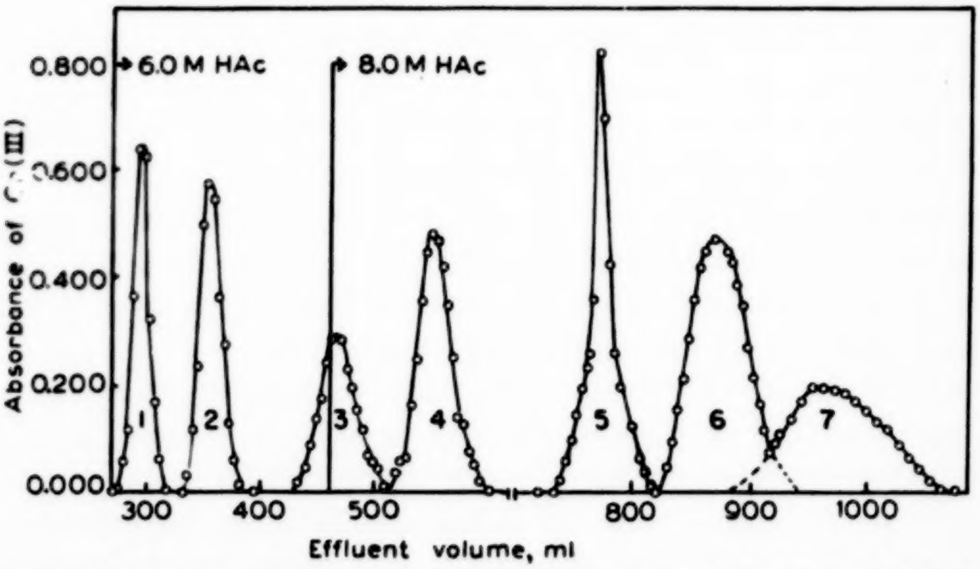

Fig. 3. Separation of a seven-component hydrocarbon mixture. 60 cm × 2.28 cm² Dowex-1-X4, 200-400 mesh, acetate form, 0.28 cm/min. Aqueous acetic acid eluent changed at 460 ml. 1. benzene; 2. toluene; 3. *m*-xylene; 4. mesitylene; 5. naphthalene; 6. β-methylnaphthalene; 7. 1,4-dimethylnaphthalene.

Consider a mixture of Dowex-50-X8, hydrogen form, 2.0 *M* acetic acid, and a very small quantity of *n*-octyl alcohol. Both acetic acid and water molecules will be uni-

TABLE IV

EFFECT OF RESIN CAPACITY ON ELUTION BEHAVIOR

Resin	*Dowex-50W-X8* *Q = 1.99 meq/g* *lot No. L3937-40* *bed = 8.3 cm × 3.9 cm²*		*Dowex-50-X8* *Q = 5.2 meq/g* *lot No. 4226-28* *bed = 21.1 cm × 3.9 cm²*	
Eluent	8.0M $HC_2H_3O_2$		6.0M $HC_2H_3O_2$	
	C	U_T	C	U_T
n-Amyl alcohol	4.57	91.6 ml	1.43	53.5 ml
n-Hexyl alcohol	7.66	193.2	1.46	70.4
n-Octyl alcohol	a	a	1.85	101.2

[a] Irreversibly adsorbed on column.
U_T = Total volume of eluent used to elute the solute completely.

formly absorbed throughout the interior of the resin particles (REICHENBERG AND WALL[10] consider the simplest explanation to be that the resin absorbs water which in turn dissolves the acetic acid). The functional groups and counter ions of the resin will no doubt be almost exclusively solvated by water molecules rather than acetic acid molecules because of the greater number and greater polarity of the former. Since this leaves less free water inside the resin in which acetic acid can dissolve, the resinate ions can be said to salt-out acetic acid from the resin phase. Also, the small chain length of acetic acid molecules indicates that little van der Waals interactions will obtain between the benzene rings of the matrix and the acetic acid molecules. Hence the molarity of acetic acid inside the resin will be lower than the molarity outside the resin[10]. Even though this is true, the small amount of octyl alcohol will go almost completely inside the resin due primarily to the strong van der Waals interactions with the resin matrix.

The separations achieved by solubilization chromatography are based on the fact that solutes are differentially dissolved from the resin phase into the outside phase. Hence, the greatest separation among a group of constituents is obtained by use of an eluent containing a small amount of acetic acid since the compounds will have the greatest relative solubility differences in such an eluent. However, the eluent must contain enough acetic acid to give narrow elution graphs.

The results cited above with low-capacity resins indicate that van der Waals forces are much more important than polar interactions between a solute molecule and the resin. The resins of low capacity have a more hydrocarbon nature than the normal resins and hence exert a greater van der Waals attraction for the organic solutes. The fewer functional groups also mean that the resin can less effectively salt the solute out of the resin phase, a factor which would also tend to increase C values. If the ion-dipole attractions were important, the C values would decrease with diminishing capacity.

Since low-capacity resins contain much less internal water than do normal resins, slower diffusion rates and tailing are to be expected. Crosslinked polystyrene contains no functional groups and cannot swell at all in aqueous solvents. In this case only surface adsorption, and not true absorption, can occur. Hence, the tailing observed with the hydrocarbons on polystyrene would be characteristic of such an adsorption phenomenon.

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SUMMARY

Synthetic mixtures of aliphatic and aromatic ethers, saturated fatty acids, and substituted benzenes and naphthalenes were separated by elution through columns of ion-exchange resins with aqueous solutions of acetic acid as eluent. An attempt was made to use a resin of low capacity for the separation of such mixtures, and the results of this attempt are used to help elucidate the theory of solubilization chromatography.

RÉUMÉS

Des mélanges d'éthers aliphatiques et aromatiques, d'acides gras saturés, de benzènes et de naphtalènes substitués ont été séparés par élution au moyen d'acide acétique sur des colonnes de résines d'échange d'ions.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Trennung von Gemischen von aliphatischen und aromatischen Aethern, gesättigten Fettsäuren und substituierten Benzolen und Naphthalinen mit Hilfe von Jonenaustauschern und Eluation mit verd. Essigsäure.

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SPECTROPHOTOMETRIC DETERMINATION OF URANIUM

APPLICATION OF THE METHOD TO THE ANALYSIS OF LEACH SOLUTIONS AND MONAZITE

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The thiocyanate method for the spectrophotometric determination of uranium, as developed by CURRAH AND BEAMISH[1], is fairly sensitive and is free from cation interferences. The major difficulties encountered when using this method appear to be due to (i) the poor colour stability, (ii) the dependence of the colour intensity on the thiocyanate concentration over a wide range and (iii) interference from a large number of anions. In a recent paper NIETZEL AND DE SESA[2] briefly reviewed the various modifications that have been introduced into the method to make it applicable to the analysis of "relatively pure uranium samples" (*i.e.* samples containing only small amounts of certain impurities) and complex materials such as ores.

The present method is based upon the extraction of the uranyl thiocyanate complex with tributyl phosphate and its spectrophotometric determination in the organic layer. Though similar methods have previously been reported in the literature[3,4] no detailed study has been made of the various factors affecting the extraction and the interferences in the subsequent determination.

After this work was completed, a report was published by CLINCH AND GUY[5] on a similar procedure, where the interference due to a number of ions was eliminated by complexing them with ethylenediaminetetraacetic acid (EDTA) at pH 3.5–3.9. The conditions under which they worked, however, were such that reagent consumption was high (about 5 g ammonium thiocyanate per estimation) and a close check had to be kept on the pH. Moreover, for the determination of uranium in ores, including monazite, they found it necessary to carry out a preliminary separation of uranium, for which they used a cellulose column. From this point of view the method described in the present paper has some advantages which are discussed in the text below.

EXPERIMENTAL

Apparatus and reagents

All colour measurements were made with a Beckman Model DU spectrophotometer using 1 cm corex cells.

The extractions were carried out in 50 ml glass stoppered separating funnels.

Unless otherwise stated AnalaR grade chemicals were used for this work.

Tributyl phosphate–carbon tetrachloride mixture. 100 ml of tributyl phosphate (TBP) (B.D.H. Laboratory Reagent) were diluted to 1 l with carbon tetrachloride, washed thrice with 250 ml portions of 10% (w/v) sodium hydroxide and then with distilled water until the washings were free from alkali. The organic layer was separated, filtered and stored.

Ammonium thiocyanate. A 2.5*M* solution was prepared and filtered.

Ascorbic acid. 5 g of ascorbic acid was dissolved in 100 ml water.

Standard uranium solution. A solution containing about 5 g U_3O_8/l was prepared by dissolving the requisite amount of uranyl nitrate and the uranium content was then accurately determined gravimetrically.

Dilute solutions containing 0.10 mg U_3O_8/ml were made from the stock solution when required.

General procedure for extraction

Solutions of uranyl nitrate, ammonium thiocyanate and ascorbic acid (to reduce traces of iron) were carefully pipetted into a beaker and the volume made up to about 25 ml. The pH was adjusted to about 1.5 and the solution transferred to a separating funnel together with the rinsings. 25.0 ml of the solvent was pipetted into the separating funnel and the mixture shaken for 2 min. The two layers were allowed to settle and the organic layer was filtered through a plug of glass wool (previously washed with hydrochloric acid to remove traces of iron and dried) into a dry test tube where it was kept stoppered till required for colour measurement.

Choice of wavelength

5 ml uranyl nitrate solution (containing 0.50 mg U_3O_8) was extracted with 25.0 ml of TBP–CCl_4 after the addition of 2.5 ml ammonium thiocyanate and 2.0 ml ascorbic acid. The optical density of the organic layer was compared at wavelengths from 330 to 400 mμ against a blank obtained by extracting a solution prepared in the same manner, but without uranium.

The absorption spectrum is similar to that obtained by CLINCH AND GUY[5] and shows a maxima at 350 mμ.

Beer's law

A series of solutions containing 0.10 to 1.50 mg U_3O_8 were extracted as described above. The optical density measurements showed that Beer's law is obeyed at 350, 365, 380 and 400 mμ and probably at any other wavelength in this region. However, since the reproducibility of the data obtained at 365 mμ was better than at lower wavelengths, this wavelength was used for all subsequent work. The molecular extinction coefficient is 5100.

Optimum concentration range for estimation

A RINGBOM plot[6] was made from the calibration data obtained at 365 mμ and the optimum range of uranium concentration for a minimum spectrophotometric error was found to be 0.20 to 1.20 mg U_3O_8 in 25 ml of the extract.

Stability of the colour

The colour in the organic extract was stable for at least 24 hours.

Factors affecting uranium extraction

To find out the effect of various factors on uranium extraction, experiments were carried out under different conditions using 0.50 mg U_3O_8. The optical density of the extract corresponding to this amount of uranium in the calibration graph (uranium concentration *vs.* optical density at 365 mμ) was assumed to represent complete extraction and on that basis the percentage extraction was calculated in the following experiments.

(*a*) *Effect of TBP concentration in the organic phase.* The extraction was almost complete (Fig. 1) when the TBP concentration in the solvent was 8% (v/v). For all further work 10% (v/v) TBP in carbon tetrachloride was used.

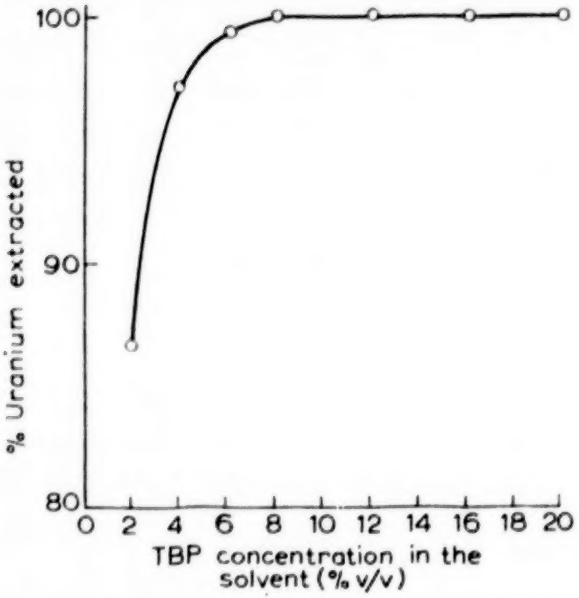

Fig. 1. Effect of TBP concentration on uranium extraction.

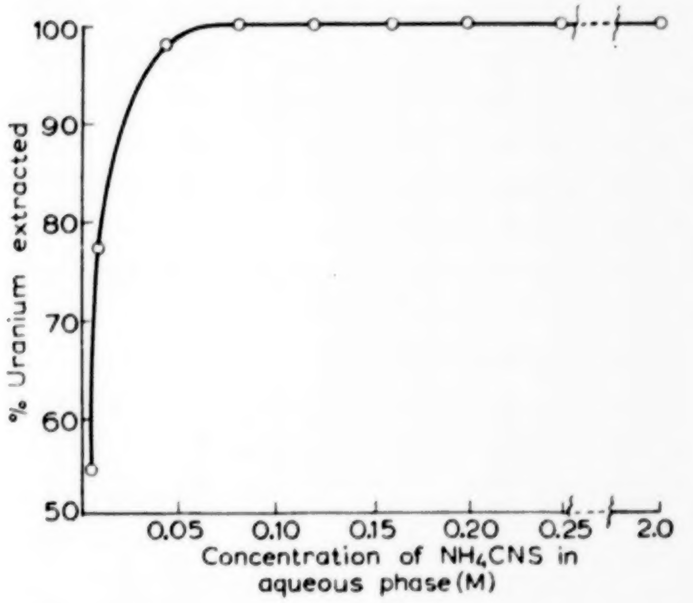

Fig. 2. Effect of thiocyanate concentration on uranium extraction.

(*b*) *Effect of thiocyanate concentration in the aqueous phase.* The extraction of uranium increased rapidly (Fig. 2) with thiocyanate concentration and reached a maximum value when the overall thiocyanate concentration was 0.1 *M*. But for various reasons, which will be mentioned later, the concentration of thiocyanate was fixed at 0.25 *M* (*i.e.* 2.5 ml of 2.5 *M* solution) for all further work.

(*c*) *Effect of pH.* Extractions carried out after adjusting the aqueous solution to various pH values showed that there was a sharp fall in uranium extraction at pH 3.5, but between 2.5 and 0.5 there was no significant difference. From highly acidic solutions some HCNS was also extracted into the organic layer which affected the stability of the colour. Throughout this work, therefore, the pH of the aqueous solution was adjusted to roughly 1.5 before extraction.

(*d*) *Interferences.* The possible interference that a number of cations and anions might have on the uranium extraction and subsequent spectrophotometric determination was evaluated. The impurities were added separately to aliquots (0.5 mg U_3O_8) of standard uranium solution and carried through the extraction and estimation procedure. The error found was less than 2% when the following ions were added up to 200 mg: Na^+, K^+, Ca^{+2}, Mg^{+2}, Cd^{+2}, Zn^{+2}, Mn^{+2}, Ni^{+2}, Al^{+3}, Cr^{+3}, La^{+3}, Ce^{+3}, Nd^{+3}, Zr^{+4}, Th^{+4} (all as chlorides or nitrates), Cl^-, NO_3^-, SO_4^{-2}, PO_4^{-3}, tartrate and citrate (all as sodium salts). The effect of some other ions is given in Table I.

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TABLE I

INTERFERENCES IN URANIUM DETERMINATIONS

Ion added	Amount of ion giving 2% error (mg)	Remarks
Co^{+2}	50	—
Pb^{+2}	20	Slight precipitate in aqueous phase
Hg^{+2}	50	Slight precipitate
Sn^{+2}	20	Turbidity in aqueous phase
Cu^{+2}	20	White precipitate of cuprous thiocyanate
Fe^{+3}	10	—
Ti^{+4}	5	0.5 g tartaric acid was also added. Otherwise less than 2 mg
V^{+5}	1	Positive error
Bi^{+3}	< 1	Positive error
Mo^{+6}	< 1	Positive error
F^-	5	Negative error
Oxalate	5	Negative error

Among the ions tested those of vanadium, bismuth, molybdenum, fluoride and oxalate proved to cause very serious interferences. Even though there was precipitate formation when some of the ions were added (Table I), the extracts were clear after filtering through the glass wool.

APPLICATION OF THE METHOD

Determination of uranium in leach solutions

On the basis of the observations described above, the method was tested for the determination of uranium in a synthetic solution (composition given below) and two leach solutions obtained by treating low-grade uranium ores with dilute sulphuric acid. The procedure was as follows.

Procedure. 2.0–5.0 ml of the leach solution was pipetted into a 50-ml beaker. 5.0 ml ascorbic acid and 2.5 ml ammonium thiocyanate were added and the solution diluted to about 25 ml. The pH was adjusted to about 1.5 and the extraction and spectrophotometric determination carried out as in the case of pure solutions. The results are summarised in Table II.

TABLE II

DETERMINATION OF URANIUM IN LEACH SOLUTIONS

Sample	Uranium present g U_3O_8/l	Aliquot taken ml	Uranium determined by the present method		
			No. of determinations made	Mean value g U_3O_8/l	Standard deviation
Synthetic solution[a]	0.211	2.0	9	0.210	0.004
Leach solution I	0.428	2.0	10	0.431	0.005
Leach solution II	0.084	5.0	8	0.083	0.001

[a] Composition (in g/l): U_3O_8 0.211, Fe^{+3} 10.0, Mn^{+2} 5.0, Cu^{+2}, Ni^{+2}, Al^{+3}, Ca^{+2}, Mg^{+2} 1.0 each, PO_4^{-3} 10.0, SO_4^{-2} 50.0. The pH was 1.0.

Determination of uranium in monazite concentrates

CLINCH AND GUY[5] determined uranium in a variety of ores, including monazite, but only after separation of uranium by the cellulose column method[7]. From the study of interferences reported above and the known composition of monazite concentrates it is evident that the present method can be applied without any preliminary separation. The following procedure was adopted and replicate analyses were carried out on a sample of monazite concentrate obtained from the Indian Rare Earths Ltd., Alwaye.

Procedure. 1.0 g of finely ground sand was mixed with about 3.0 ml concentrated sulphuric acid in a 50 ml beaker and heated for about 2 hours at a temperature just below the fuming stage. After cooling, the sulphates were extracted with ice-cold water, the solution transferred to a 50 ml volumetric flask and, after it had attained room temperature, made up to the mark. The solution was mixed occasionally and after 2 hours filtered through a dry Whatman No. 42 filter.

10 ml of the filtrate was carefully pipetted into a separating funnel, 2.5 ml thiocyanate, 5 ml ascorbic acid and about 10 ml water were added and the extraction and determination of uranium carried out.

Results: U_3O_8 present 0.406% (by cellulose column method[7])
U_3O_8 found 0.403% (mean of 10 determinations by present method)
Standard deviation: 0.014.

DISCUSSION

From the results reported it can be seen that extraction of the thiocyanate complex with TBP and subsequent spectrophotometric determination is a very convenient and rapid method for the determination of uranium in leach solutions, not containing vanadium, bismuth and molybdenum. The use of ascorbic acid, instead of EDTA for eliminating certain interferences offers an advantage in that the extraction of uranium is complete over a wide range of pH values of the aqueous phase; moreover, the reagent consumption is very much less and a lower concentration of TBP in the solvent can be used. Because of the acid conditions (pH 1.5 or less) employed there is no trouble due to precipitation of phosphates of uranium, thorium or hydrolysis of zirconium. The intensity of the colour is to a large extent independent of the thiocyanate concentration in the aqueous phase. Although, under the conditions employed, the extraction from pure uranium solutions is complete at a thiocyanate concentration of $0.1M$, a slightly higher concentration, *i.e.* $0.25M$, is generally employed to overcome the interference from anions such as SO_4^{-2} and PO_4^{-3}.

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SUMMARY

Uranyl thiocyanate complex is extracted from a slightly acid solution, using tributyl phosphate–carbon tetrachloride as solvent. The effect of various factors on the extraction of uranium and the interference of a number of cations and anions was studied. After extraction, uranium is determined spectrophotometrically in the organic solvent.

RÉSUMÉ

On propose une méthode de dosage spectrophotométrique de l'uranium. Elle est basée sur l'extraction du thiocyanate complexe au moyen du mélange phosphate de tributyle–tétrachlorure de carbone. L'influence d'un certain nombre de cations et d'anions a été examinée.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Methode zur Bestimmung von Uran beschrieben. Sie beruht auf der Extraktion des Uranyl-thiocyanat Komplexes mit einem Gemisch von Tributylphosphat und Tetrachlorkohlenstoff. Der Einfluss einer Anzahl Kationen und Anionen wird untersucht.

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OXIDATION OF HYDROXYLAMINE BY FERRICYANIDE IN PRESENCE OF ZINC SULFATE

A RAPID METHOD FOR ESTIMATING HYDROXYLAMINE AND HYDRAZINE IN A MIXTURE

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Both hydrazine and hydroxylamine are powerful reducing agents and their determination in presence of each other is usually a difficult problem. While hydrazine is almost always oxidized exclusively to nitrogen by various reagents, hydroxylamine tends to be converted non-stoichiometrically to several products such as N_2, N_2O, HNO_2, HNO_3 and other related compounds[1]. Nonetheless, under prescribed conditions, hydroxylamine is oxidized to nitrous oxide by cerium(IV)[2] and iron(III)[3], to nitric acid by bromate[4], and to nitrogen by ferricyanide[5]. The standard method of determining hydroxylamine is based on its conversion to nitric acid by an excess of potassium bromate in hydrochloric acid solution followed by an iodometric titration of the excess against thiosulfate[4]. Experience has shown that the bromate method requires considerable skill and rigid adherence to the prescribed conditions, especially in preventing the loss of free bromine which is formed during the reaction. FURMAN AND

FLAGG[6] have suggested a useful modification of this procedure by adding an excess of standard arsenite solution to the unreacted bromate, and backtitrating with 0.1 N bromate using methyl orange indicator. The results by this modification were found to be much better than by direct iodometry of the excess of bromate, but the method is still involved. Perhaps it might be preferable to use a bromate–bromide mixture in strongly hydrochloric acid or glacial acetic acid medium.

In the literature, two methods are described for the determination of hydrazine and hydroxylamine when present together. Potassium bromate in hydrochloric acid solution oxidizes hydrazine and hydroxylamine respectively to nitrogen and nitric acid. The excess of bromate is determined in one sample whereas in the second sample the volume of nitrogen evolved is measured[7]. According to LANG[8], hydrazine can be titrated in sulfuric acid solution with potassium iodate by the iodine cyanide procedure without oxidation of hydroxylamine, provided that not more than the equivalent of 0.07 g of $NH_2OH{\cdot}HCl$ are present. After the ICN is destroyed by just a sufficient quantity of sodium sulfite, the iodide ion is precipitated with silver nitrate. The hydroxylamine is then oxidized to nitrous oxide and water by boiling with an excess of ferric ammonium sulfate, and the iron(II) formed is titrated in presence of manganous sulfate catalyst with standard permanganate. While the former method necessitates a gasometric measurement, the latter is a lengthy procedure and is dangerous owing to the use of potassium cyanide.

SANT[5,9] developed a method of determining hydroxylamine, based on its conversion to nitrogen by an excess of ferricyanide in a weakly alkaline solution (pH 8–9). The analysis was completed by titrating the ferrocyanide formed with ceric sulfate or the unused ferricyanide iodometrically. In strongly alkaline medium the reaction is non-stoichiometric. Recently it has been shown that hot standard solutions of ferricyanide can be titrated directly with hydrazine sulfate[10] or sodium nitrite[11] in presence of zinc sulfate. Zinc sulfate raises the oxidation potential of the ferricyanide ion through the removal of ferrocyanide ion as sparingly soluble zinc potassium ferrocyanide. The complete decolorization of the solution indicates the end-point.

Preliminary experiments in these Laboratories revealed that the above ferricyanide procedures for hydrazine and nitrite could be extended to determine hydroxylamine. However, in presence of zinc sulfate, hydroxylamine is oxidized to nitric acid instead of to nitrogen as when ferricyanide is used in a weakly alkaline medium. Ferricyanide in strongly alkaline solutions or in presence of zinc sulfate always converts hydrazine to nitrogen so that oxidation of a sample containing both hydrazine and hydroxylamine by ferricyanide under different conditions should give a measure of the quantity of each reductant present. Ferricyanide in strongly alkaline medium does not convert hydroxylamine quantitatively to nitrogen but no data exist on the reaction between hydrazine and ferricyanide in weakly alkaline medium. A series of experiments showed that hydrazine is oxidized quantitatively to nitrogen by excess of ferricyanide in borax–boric acid buffer solution (pH 8–9). The analysis was completed by titrating both the ferrocyanide formed against standard ceric sulfate[12] and the unused ferricyanide iodometrically against standard thiosulfate[13]. These observations were used in the present work.

The present paper reports a simple method of determining milligram amounts of hydroxylamine by direct titration of alkaline ferricyanide in presence of zinc sulfate and a rapid procedure for the analysis of hydroxylamine and hydrazine when present together.

EXPERIMENTAL

An aqueous solution of hydroxylamine sulfate was prepared from a pure sample supplied by the Commercial Solvents Corporation. Its hydroxylamine content was checked by titrating the acid part and also by the ferricyanide method[5,9]. All other chemicals used were of reagent grade.

Procedure

Determination of hydroxylamine. To a measured volume of standard potassium ferricyanide solution, 2–3 g of crystalline zinc sulfate and a sufficient quantity of sodium or potassium hydroxide to maintain the total alkalinity at 0.5–1.0N were added and the mixture was heated to boiling. The hydroxylamine sulfate solution was added from a buret gradually till the precipitate was clear white and the supernatant liquid colorless. The reaction corresponds to the oxidation of hydroxylamine to nitric acid and water:

$$2K_3Fe(CN)_6 + 2KOH \rightarrow 2K_4Fe(CN)_6 + H_2O + [O]$$

$$2K_4Fe(CN)_6 + 3ZnSO_4 \rightarrow Zn_3K_2[Fe(CN)_6]_2 + 3K_2SO_4$$

$$NH_2OH + 3[O] \rightarrow HNO_3 + H_2O$$

Thus 1 ml of 1N $K_3Fe(CN)_6$ is equivalent to 5.505 mg NH_2OH. A typical set of results is given in Table I.

TABLE I

ESTIMATION OF HYDROXYLAMINE

NH_2OH (mg)		*Difference (mg)*
Calculated	*Found*	
1.114	1.101	0.013
2.228	2.203	0.025
4.456	4.407	0.049
8.912	8.818	0.094
13.368	13.224	0.144

Determination of hydroxylamine in presence of hydrazine. Measured quantities of hydroxylamine and hydrazine sulfates were mixed and the solution diluted to 250 ml. Oxidation was effected by ferricyanide as follows:

(*a*) An aliquot portion of the mixture was treated with a known excess of ferricyanide solution followed by 25–30 ml of borax–boric acid buffer solution (pH 8–9). After 15–30 min, the solution was diluted to a suitable volume. In aliquots of this solution either the unused ferricyanide was titrated iodometrically or the ferrocyanide formed was titrated with standard ceric sulfate.

(*b*) A known volume of ferricyanide was titrated hot in presence of zinc sulfate and at a total alkalinity of 0.5–0.8N with the mixed solution of hydrazine and hydroxylamine sulfates. The end-point was shown by the appearance of a clear white precipitate.

In the two methods (*a*) and (*b*), the reactions taking place are:

$$(a)\quad N_2H_4 + 4K_3Fe(CN)_6 + 4KOH \rightarrow N_2 + 4K_4Fe(CN)_6 + 4H_2O \quad \ldots\ldots \quad (1)$$

$$2NH_2OH + 2K_3Fe(CN)_6 + 2KOH \rightarrow N_2 + 2K_4Fe(CN)_6 + 4H_2O \quad \ldots \quad (2)$$

$$(b)\quad N_2H_4 + 4K_3Fe(CN)_6 + 4KOH + 6ZnSO_4 \rightarrow N_2 + 2Zn_3K_2[Fe(CN)_6]_2 + 6K_2SO_4 + 4H_2O \quad \ldots\ldots \quad (3)$$

$$NH_2OH + 6K_3Fe(CN)_6 + 6KOH + 9ZnSO_4 \rightarrow HNO_3 + 3Zn_3K_2[Fe(CN)_6]_2 + 9K_2SO_4 + 4H_2O \quad \ldots\ldots \quad (4)$$

Let V_1 and V_2 be the volumes of ferricyanide consumed by the same quantity of the mixture in methods (*a*) and (*b*) respectively. If x ml of ferricyanide are consumed by hydrazine, then $(V_1 - x)$ ml will have been consumed by hydroxylamine in (*a*) and $(V_2 - x)$ ml in (*b*). Whereas the equivalent weight of hydroxylamine in (*a*) is the same as the molecular weight, it is one-sixth in (*b*). Therefore

$$(V_1 - x) = \frac{(V_2 - x)}{6}$$

From this the values of x, $(V_1 - x)$, and $(V_2 - x)$ can be obtained. The quantity of hydrazine equivalent to x ml of ferricyanide can be calculated from the relation 1 ml of $1N$ $K_3Fe(CN)_6 = 8.012$ mg hydrazine and the hydroxylamine equivalent of $(V_2 - x)$ ml of ferricyanide from the relation 1 ml of $1N$ $K_3Fe(CN)_6 = 5.505$ mg hydroxylamine.

RESULTS

A representative set of data is shown in Table II. The results are the average values of duplicate experiments.

TABLE II

ESTIMATION OF HYDRAZINE AND HYDROXYLAMINE IN A MIXTURE

Expt. No.	*N_2H_4 (mg)*			*NH_2OH (mg)*		
	Calcd.	*Found*	*Diff.*	*Calcd.*	*Found*	*Diff.*
1.	3.174	3.186	0.012	0.9635	0.9545	0.009
2.	1.440	1.450	0.010	1.927	1.909	0.018
3.	6.348	6.362	0.014	1.927	1.909	0.018
4.	1.440	1.450	0.010	3.854	3.820	0.034
5.	2.880	2.900	0.020	3.854	3.818	0.036
6.	2.880	2.900	0.020	7.708	7.640	0.068

DISCUSSION

The reaction between ferricyanide and hydroxylamine in presence of zinc sulfate was shown to be quantitative at an alkalinity of 0.5–1.0*N*. At lower alkalinity the reaction is slow, whereas in too alkaline a solution zinc ions tend to go into solution and interfere with reaction(4). This difficulty can be obviated by using larger quantities of zinc sulfate. The amount of zinc sulfate is not critical provided that more than 2 g are present during each titration.

When hydroxylamine is oxidized to nitric acid, a good conversion factor is obtained so that the method is suitable for the determination of small amounts of hydroxylamine. Potassium bromate also effects this oxidation completely, but the present ferricyanide method is simpler and much less time-consuming. The availability of very pure potassium ferricyanide and its large equivalent weight (about 12 times that of potassium bromate) are also important.

In contrast to the bromate and the iodine cyanide methods for analyzing a mixture of hydrazine and hydroxylamine, the ferricyanide procedure described is not exacting and it can be completed within 45 minutes. The error rarely exceeds 2% which may be acceptable considering the difficulties involved in such an analysis.

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SUMMARY

The direct titration of alkaline ferricyanide in presence of zinc sulfate with hydroxylamine sulfate has been studied. A clear white precipitate of zinc potassium ferrocyanide indicates the end-point. Hydroxylamine is oxidized to nitric acid and water, and milligram quantities of hydroxylamine can be determined. In the absence of zinc sulfate and in weakly alkaline medium, hydrazine and hydroxylamine are converted to nitrogen, while in presence of zinc sulfate hydrazine is oxidized to nitrogen. By ferricyanide oxidation of a mixed sample under different conditions, hydrazine and hydroxylamine when present together can be determined rapidly.

RÉSUMÉ

L'auteur décrit une méthode simple pour le microdosage de l'hydroxylamine, au moyen de ferricyanure, en présence de sulfate de zinc. Il propose également une méthode rapide pour le dosage de l'hydrazine et de l'hydroxylamine, en présence l'une de l'autre, par le ferricyanure de potassium, avec et sans sulfate de zinc.

ZUSAMMENFASSUNG

Es wird eine einfache Mikromethode beschrieben zur Bestimmung von Hydroxylamin mit Alkaliferricyanid in Gegenwart von Zinksulfat. Unter Einhaltung bestimmter Bedingungen können auch Hydroxylamin und Hydrazin nebeneinander mit Alkaliferricyanid bestimmt werden.

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THE APPARENT SOLUBILITY PRODUCT OF CEROUS FLUORIDE

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The present work grew out of an as yet unsuccessful attempt to determine fluoride ion coulogravimetrically with electrolytically generated cerous ion. Although cerous ion could be generated with 100% current efficiency from an acid solution of a ceric salt, in the presence of fluoride ion no visible precipitate was noted. Two causes are possible for this lack of precipitate: (a) the high solubility of cerous fluoride in acid solution and (b) the slow formation of precipitate under these conditions. The former possibility is the subject of the present paper.

No experimental data are available on the solubility product of cerous fluoride[1] although KURY[2] has calculated this constant from thermodynamic data. The apparent solubility product has now been determined by two independent methods and the values obtained checked fairly closely. However, these values are some 700 times larger than the calculated value. The solubility of cerous fluoride in solutions of varying acidity has also been determined.

REAGENTS AND APPARATUS

The reagents used were all of "analytical grade". The tracer employed was an acid solution of cerium-144(III) chloride and was obtained from Oak Ridge National Laboratory. Conductivity water was prepared by distillation in all-glass apparatus after the addition of a few crystals of potassium permanganate. The freshly distilled water was then passed through a Crystalab Deeminizer deionizing column. The water thus prepared was stored in polyethylene bottles and was used for the preparation of all solutions employed in the conductometric measurements. Due to the absorption of carbon dioxide, the conductivity of the water increased rapidly but within 8 min showed no further change, even after 24 h. All runs were made with equilibrium water having a specific conductance of $4.5 \cdot 10^{-6}$ mho.

Conductance measurements were made with a standard Wheatstone Bridge circuit; earphones were used as the null-detecting device and the 1000-cycle a.c. was obtained from a Jackson Model No. 652 audio frequency oscillator. The constant of the cell was 0.05398. Radioactive counting was by a Tracerlab TGC-5A Geiger tube and an Atom-lab Model A-65 scaler. All samples were mounted on polystyrene planchettes.

A Burrel Model BB Wrist Action Shaker was used to bring the solid cerous fluoride into equilibrium with its medium. All pH measurements were made on a Beckman Model H2 glass-electrode pH Meter.

EXPERIMENTAL PROCEDURES

Radioactive cerous fluoride was prepared by adding three drops of cerium-144(III) chloride to 20 ml of a 0.1*N* solution of cerous sulfate (G. Frederick Smith Chemical Co., Columbus, Ohio). This solution was then added dropwise with constant stirring to 20 ml of 0.1*N* sodium fluoride. The precipitate was allowed to stand for 30 min before filtration. It was then washed and dried at 110° for 3 h.

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A 200-mg sample of active cerous fluoride was placed in a 25-ml volumetric flask and water was added to bring to the mark. The flask was shaken and maintained at 25° ± 0.05° for 18 h to allow the cerous fluoride to come to equilibrium with the medium. At the end of this period, the mixture was filtered and an aliquot of the filtered solution was pipetted into a planchette and evaporated to dryness under a Fisher Radiator.

The solubility of cerous fluoride in solutions of varying acidity was determined as above except that perchloric acid solutions of known pH replaced the distilled water. Perchloric acid was chosen as it does not complex with cerous ion[3].

For conductometric measurements, 20 ml of approximately 0.1 N cerous sulfate solution was added dropwise with constant stirring to an equal volume of 0.1 N sodium fluoride. The precipitate was allowed to settle and the supernatant liquid was decanted. After washing with six 5-ml portions of conductivity water, 200-mg portions of the dried salt were placed in each of six polyethylene bottles containing 20 ml of conductivity water. The bottles were shaken and thermostatted as before. The mixture was filtered through a fine filter paper and the filtrate was used to rinse the cell before conductance measurements were made.

RESULTS

Solubility product measurements

The apparent solubility product of cerous fluoride was determined by radiometric and conductometric methods to be $8.1 \pm 1.1 \cdot 10^{-16}$ and $1.1 \pm 0.5 \cdot 10^{-15}$ respectively. These values are somewhat larger than the value of $1.4 \pm 0.2 \cdot 10^{-18}$ reported by KURY.

For conductometric measurements, the equivalent conductance was assumed to be equal to the equivalent conductance at infinite dilution. The ionic conductance of fluoride ion is reported to be 46.6 mhos/equivalent at 18° and can be corrected for temperature by use of the following equation:

$$\lambda_{t'} = \lambda_t(1 + c(t' - t))$$

where c is 0.0238, t' is the desired temperature, and t is 18°[4]. Since no information is available on the equivalent ionic conductance of cerous ion, the value for the lanthanum ion was used. The ionic radii of the lanthanum and cerous ions are similar, 1.15 and 1.18 Å respectively[5]. Ions having the same charge and similar ionic radii are known to have similar mobilities and equivalent ionic conductances[6].

Uncertainties in the conductance method are (a) the nature of the ions formed, (b) the values of the ionic conductances, and (c) the extent of salt hydrolysis. Complexing of cerous ion by fluoride to form the species CeF^{+2} has been proposed by KURY, HUGUS AND LATIMER[7]. The formation of a cerium–fluorine complex would increase the solubility product. However, the value obtained after correction for complex formation is still well within the limits of experimental error. Calculations of the solubility product based on the assumption that salt hydrolysis had taken place gave values which were much greater than any experimental value obtained. This suggests that salt hydrolysis must also be very small.

Variation of solubility with acidity

The radiometric method was used to study the effect of hydrogen-ion concentration on the solubility of cerous fluoride. The results in Fig. 1 show that the solubility decreases very gradually with a decrease in pH from 5 to 2 and then increases rapidly as the pH is further reduced from 2 to 0. Three factors should be considered in explaining these results, the effect of (a) a strong acid on the solution of the salt of a weak acid, (b) increased ionic strength in the more acid solutions, and (c) the deviation from Debye-Hückel behavior when the solution can no longer be considered dilute. The decrease in solubility between pH 5 and 2 may be explained as the deviation from the Debye-Hückel equation. Between pH 2 and 0 the first and second factors seem to predominate. Calculations employing the ionization constant of hydrogen fluoride indicate that a simple explanation as proposed in part (a) above is not of itself adequate.

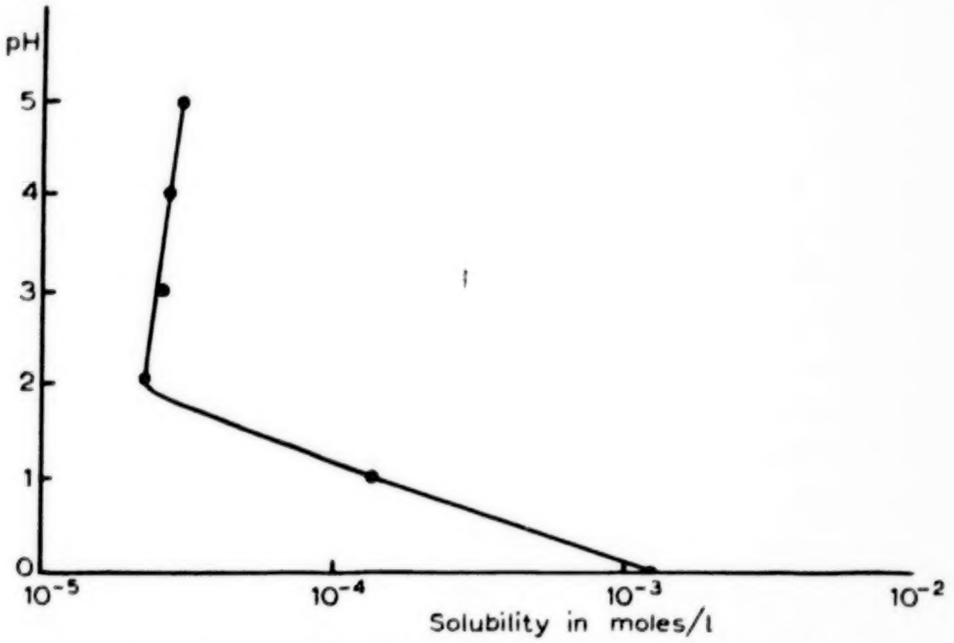

Fig. 1. pH-solubility relationship for cerous fluoride.

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SUMMARY

The apparent solubility product of cerous fluoride has been determined to be $8.1 \pm 1.1 \cdot 10^{-16}$ and $1.1 \pm 0.5 \cdot 10^{-15}$ by radiometric and conductometric methods respectively. Hydrolysis of cerous fluoride is thought to be negligible. The effect of hydrogen-ion concentration on the solubility of cerous fluoride has been measured in solutions of perchloric acid of varying acidity. The solubility was found to decrease slightly as the pH decreased from 5 to 2 and then to increase rapidly as the pH further decreased from 2 to 0.

RÉSUMÉ

Le produit de solubilité apparent du fluorure de cérium(III) a été déterminé par des méthodes radiométriques et conductométriques. L'influence du pH sur la solubilité de ce sel a été examinée.

ZUSAMMENFASSUNG

Es wird über die Bestimmung des wahrscheinlichen Löslichkeitsproduktes des Cer(III)-fluorids mit Hilfe von radiometrischen- und konduktometrischen Methoden berichtet und der Einfluss des pH auf die Löslichkeit dieser Verbindung untersucht.

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SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM

III. A COMPARATIVE STUDY OF 2-MERCAPTOBENZOTHIAZOLE AND 2-MERCAPTOBENZIMIDAZOLE AS ANALYTICAL REAGENTS

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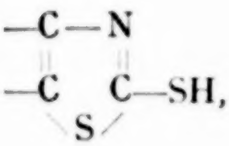
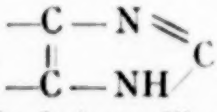
Spectrophotometric determinations of palladium with bismuthiols have already been discussed[1]. The palladium–bismuthiol complexes do not show any sharp peaks of maximum absorption, though density measurements at 400–410 mμ with bismuthiol I and 410–430 mμ with bismuthiol II establish their adherence to Beer's law at palladium concentrations of 0.8 to 8.0 μg/ml and 0.4 to 8.0 μg/ml respectively. Bismuthiol II complex, with the metal to reagent ratio of 1:2, is more stable ($K = 2.8 \cdot 10^{-12}$) compared to bismuthiol I complex ($K = 3.2 \cdot 10^{-5}$), where the metal to reagent ratio is 1:1.

The reagents, 2-mercaptobenzothiazole[2,3],  and 2-mercaptobenzimidazole[3-5],  having the same reactive mercapto groups as the bismuthiols, behave likewise in their reactions with palladium and are more akin to bismuthiol II. The red coloured complexes of the reagents with palladium give yellow to orange coloured systems while in solution of 10% alcohol or acetone. The reagents and the colour systems show high absorption in the ultraviolet region and less high in the visible, where they have no sharp peak of maximum absorption. The colour intensity of the complexes has, therefore, been measured at those regions of maximum absorption, where the reagents have minimum absorption.

The wave length used for the measurements of optical density of the systems at the optimum pH range of 3 to 6.5 is 380 mμ and at this wave length Beer's law has been found to hold good at palladium concentrations of 0.4–6.0 μg/ml. The corresponding optimum range, evaluated according to RINGBOM's method[6], is 1.6–4.0 μg/ml and the per cent relative analytical error, according to AYRES[7], per 1% absolute photometric error is 3.0. The respective sensitivities in μg of palladium per cm^2 for 2-mercaptobenzothiazole and 2-mercaptobenzimidazole are 0.06 and 0.07 (practical); 0.011 and 0.013 at 380 mμ (SANDELL[8]).

The colour systems are stable for over 24 h and are unaffected by excess reagent and by variations of temperature from 20° to 30°. Complexone III, which has no influence on the colour reaction or on the intensity of the colour, masks the interfering effects of a large number of ions. The presence of more than 10% of alcohol or acetone reduces the intensity, and the ions of gold, platinum, copper, chromium, mercury, silver, thallium, uranium, vanadate and cyanide interfere with the determination of palladium.

Job's method of continuous variation indicates that in solution the complexes contain palladium and the reagent in ratios of 1:2 with dissociation constants in the order of 10^{-12}.

EXPERIMENTAL

Apparatus and solution

The reagents, 2-mercaptobenzothiazole and 2-mercaptobenzimidazole, were prepared and crystallised according to described methods[2,4,5]. A 0.2% aqueous solution of 2-mercaptobenzimidazole and a 0.2% solution of 2-mercaptobenzothiazole in dilute aqueous alkali were prepared and used as colour-forming reagents.

Solutions of palladium, of other cations and anions, and of complexone III and the organic solvents were the same as stated in previous communications[1]. Equimolecular and non-equimolecular solutions of palladium and the reagents were prepared for the study of the composition and the dissociation constants of the complexes.

The Unicam SP 600 spectrophotometer with 1 cm cell and the Cambridge pH indicator were the same as used previously.

Colour reaction

Both the reagents react instantaneously with palladium to produce red precipitates which are less soluble in water but dissolve easily in presence of ethyl alcohol or acetone. Thus stable colour systems were made by the addition of either of the said solvents (preferably ethyl alcohol due to its comparatively low volatility) to the extent of only 10% (v/v) of the total volume. An excess of the organic solvents usually reduces the colour intensity. Complexone III, which masks the influences of other ions, does not affect the colour reaction if only 50 mg of it is present in a total volume of 25 ml.

Fig. 1 represents the absorbance curves of the colour systems (I) of palladium complex against the reagent solutions, (II) of the palladium complex against water and (III) of reagent solution against water. The curves indicate that the optical densities of the reagents decrease sharply from 360 mμ and are almost negligible after 380 mμ, while the palladium complexes exhibit practically the same absorption between 380 and 390 mμ, and hence all measurements were made at 380 mμ.

For the density measurements, the colour systems with 2-mercaptobenzothiazole and 2-mercaptobenzimidazole were maintained at pH 4.2 and 3.6 respectively and contained, besides palladium, 2 ml of the reagent and 2.5 ml of ethyl alcohol in a total volume of 25 ml.

Effect of reagent, pH, time and temperature

The absorption study at 380 mμ of a number of solutions each with 4 μg of palladium per ml and with different quantities of any of the reagents (1 to 10 ml) and maintained at a pH of 5.0 (for 2-mercaptobenzothiazole) or 4.2 (for 2-mercaptobenzimidazole) reveals that the presence of an excess of the reagent has no adverse effect.

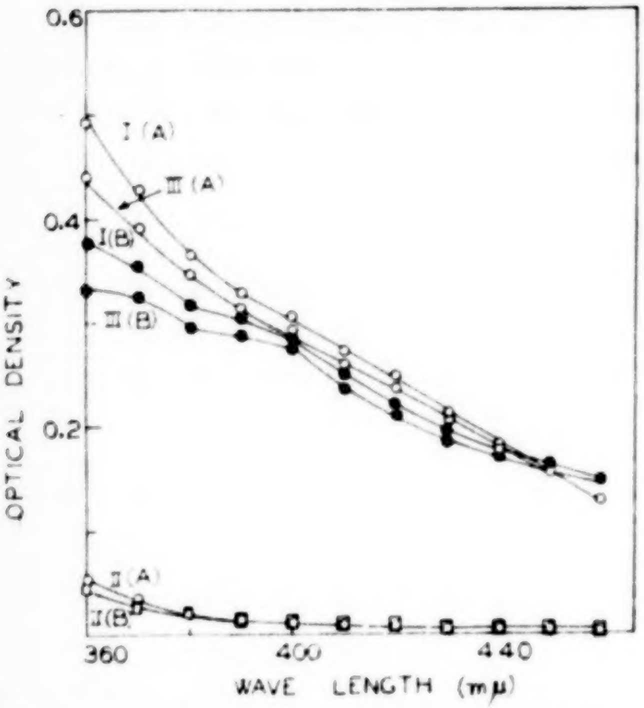


Fig. 1. Absorption regions of the colour systems. (A) 2-Mercaptobenzothiazole; (B) 2-Mercaptobenzimidazole; I 4 μg of Pd per ml, II without Pd, III corrected values.

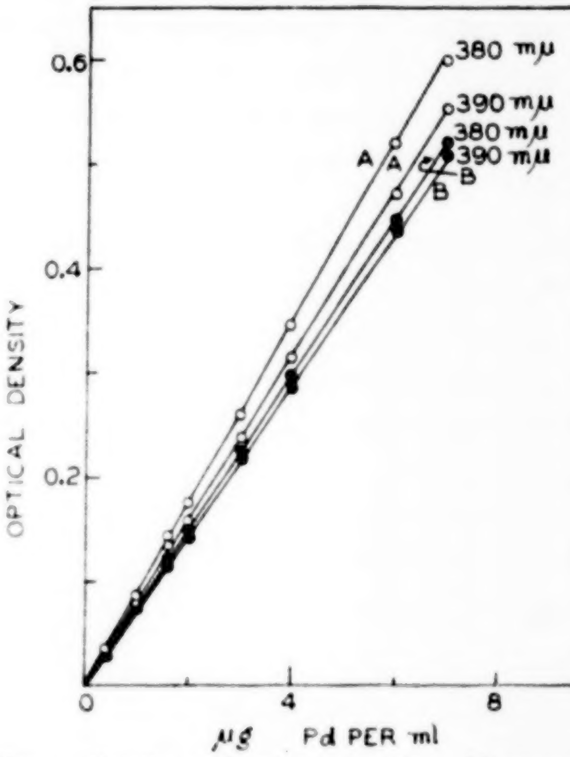


Fig. 2. Study of Beer's law. (A) 2-Mercaptobenzothiazole; (B) 2-Mercaptobenzimidazole.

Similar studies with a number of coloured systems each adjusted to a definite pH show that the colour intensity as measured against a reagent blank remains practically unchanged for 24 h over the pH range of 3 to 6.5. It even remains unaffected when the temperature of the systems is varied between 20° and 30°, but at 35° a deviation of only 1% is observed.

Beer's law and sensitivity

The colour systems with 0.4 to 6.0 μg of palladium per ml were found to obey Beer's law as, when the optical densities at 380 and 390 mμ were plotted against the respective concentrations of palladium, straight lines which pass through the origin were obtained (Fig. 2).

With 2-mercaptobenzothiazole, the optical densities for 4 μg of palladium per ml are 0.345 and 0.312 respectively at 380 mμ and 390 mμ and the sensitivity of the colour reaction is 0.066 μg of palladium per cm^2 (practical); being 0.011 μg and 0.013 μg of palladium per cm^2 at 380 mμ and 390 mμ respectively (SANDELL).

With 2-mercaptobenzimidazole, for the same amount of palladium per ml, the optical densities are 0.296 and 0.287 at 380 mμ and 390 mμ respectively and the sensitivity of the colour reaction is 0.07 μg of palladium per cm^2; sensitivity values according to SANDELL are 0.013 μg and 0.014 μg of palladium per cm^2 at 380 mμ and 390 mμ respectively.

For Beer's law, optical density was measured against a reagent blank and the systems at pH 5.0 contained, in a total volume of 25 ml, 0.4 to 10.0 µg of palladium per ml, 4 ml of the reagent and 2.5 ml of ethyl alcohol.

Evaluation of optimum range of Beer's law and the accuracy in photometric analysis

The optimum concentration range and the accuracy of the photometric analysis are evaluated on plotting 'per cent absorption' as the ordinate against 'log concentration' as the abscissa (Fig. 3). Accuracy is greatest where the curve has its steepest slope. Thus the suitable range with the minimum error is in the region of 1.6 to 4.0 µg of palladium per ml, when the measurements are made at 380 mµ.

Per cent relative error per 1% absolute photometric error

The per cent relative error ((dc/c × 100) per 1% photometric error has been calculated and plotted against the transmission. Thus it is found that the measurements of the optical density of the systems can be made with the minimum error at 30.1% transmission with 2-mercaptobenzothiazole and at 35.8% transmission with 2-mer-

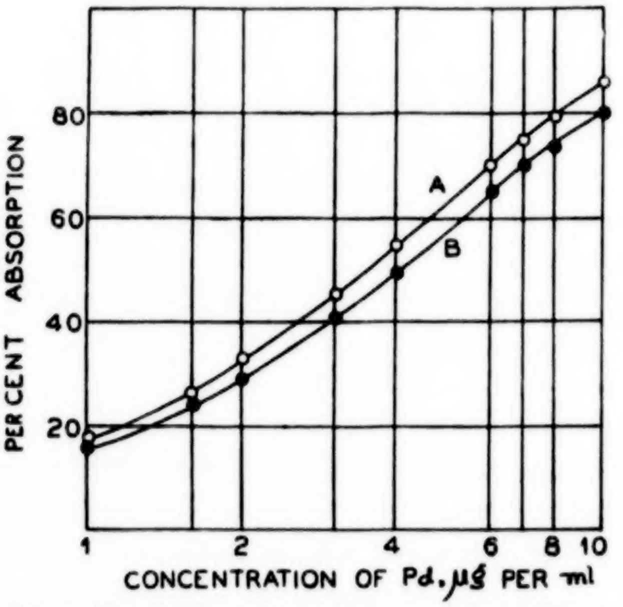


Fig. 3. Evaluation of optimum range of Beer's law. (A) 2-Mercaptobenzothiazole; (B) 2-Mercaptobenzimidazole.

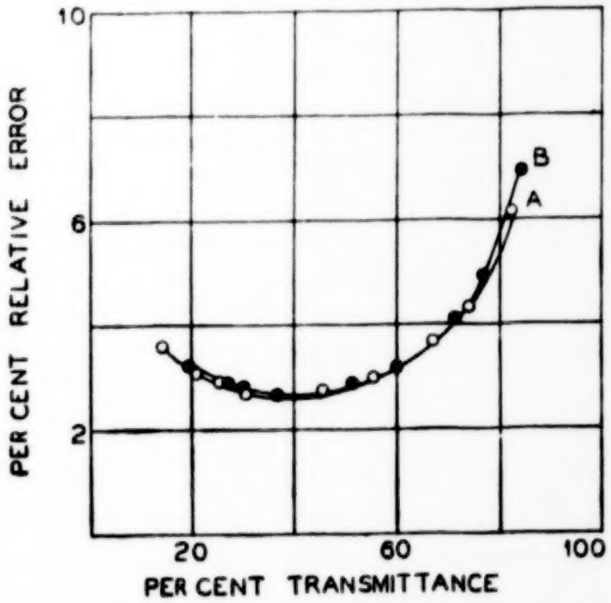


Fig. 4. Evaluation of relative error. (A) 2-Mercaptobenzothiazole; (B) 2-Mercaptobenzimidazole.

TABLE I

EVALUATION OF THE RELATIVE ERROR IN THE SYSTEM WITH 2-MERCAPTOBENZOTHIAZOLE

Concn. of Pd µg/ml	*Transmission*	$\frac{dc}{c}$ × 100 (*% relative error per 1% photometric error*)
1.0	82.0	6.2
1.6	73.3	4.4
2.0	66.9	3.7
3.0	54.9	3.0
4.0	45.2	2.8
6.0	30.1	2.7
7.0	25.1	2.9
8.0	20.8	3.1
10.0	14.1	3.6

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captobenzimidazole (Fig. 4). Tables I and II show the variation of the analytical error with the transmission.

TABLE II

EVALUATION OF THE RELATIVE ERROR IN THE SYSTEM WITH 2-MERCAPTOBENZIMIDAZOLE

Concn. of Pd µg/ml	*Transmission*	$\frac{dc}{c} \times 100$ *(% relative error per 1% photometric error)*
1.0	84.1	6.9
1.6	76.4	4.9
2.0	71.1	4.1
3.0	59.7	3.2
4.0	50.6	2.9
6.0	35.8	2.7
7.0	30.1	2.8
8.0	26.3	2.9
10.0	19.3	3.2

TABLE III

INTERFERING EFFECT OF DIVERSE IONS

palladium taken, 100 µg

Ions	*Maximum amount tolerated µg*	*Ion/Pd ratio at maximum tolerance limit*	*Ions*	*Maximum amount tolerated µg*	*Ion/Pd ratio at maximum tolerance limit*
Ca^{+2}	200	50.0	Fe^{+3}	80	20.0
Ba^{+2}	200	50.0	Cl^-	250	62.5
Sr^{+2}	200	50.0	F^-	400	100.0
Mg^{+2}	200	50.0	Br^-	200	50.0
Co^{+2}	40	10.0	I^-	200	50.0
Mn^{+2}	100	25.0	NO_3^-	250	62.5
Ni^{+2}	40	10.0	NO_2^-	200	50.0
Zn^{+2}	100	25.0	SO_4^{-2}	200	50.0
Al^{+3}	100	25.0	$S_2O_3^{-2}$	200	50.0
Be^{+2}	50	12.5	PO_4^{-3}	200	50.0
Th^{+4}	120	30.0	AsO_4^{-3}	160	40.0
Zr^{+4}	140	35.0	AsO_3^{-3}	160	40.0
TiO_2^{+2}	50	12.5	BO_3^{-3}	200	50.0
Pb^{+2}	100	25.0	MoO_4^{-2}	100	25.0
Cd^{+2}	100	25.0	WO_4^{-2}	100	25.0
Bi^{+3}	100	25.0	Acetate	200	50.0
Sn^{+4}	40	10.0	Formate	250	62.5
Ru^{+3}	8	2.0	Oxalate	200	50.0
Os^{+4}	8	2.0	Benzoate	160	40.0
Ir^{+4}	8	2.0	Salicylate	160	40.0
Rh^{+3}	2	0.5	Citrate	200	50.0
Sb^{+3}	50	12.5	Tartrate	200	50.0

Procedure

On the basis of the results of the experiments, the following procedure is recommended.

Add to the palladium solution in succession 2 ml of the reagent solution and 2.5 ml of ethyl alcohol, and adjust its pH in such a way that on dilution with water to 25 ml, it remains between 3 and 6.5. After thorough mixing at 20°–25°, place the solution in a 1 cm cell and measure its optical density at 380 mμ. Similarly, prepare a reagent blank and measure its optical density.

Effect of diverse ions

The interfering effect of the ions was studied by means of the colour intensity produced on the addition of the solution of ion to the solution of palladium (100 μg) taken in a 25 ml-flask with 2.5 ml of 1% complexone III solution, 2 ml of the reagent and 2.5 ml of ethyl alcohol. After the adjustment of its pH, the solution was diluted to 25 ml as suggested above and its optical density in a 1-cm cell, at 20°–25°, was measured at 380 mμ against a reagent blank. An ion is considered to interfere if the absorbance differs by more than 0.005 from the value obtained in its absence. Tolerance limits for the ions are summarised in Table III. The ions of gold, platinum, copper, silver, mercury, thallium, chromium, uranium, vanadate and cyanide interfere.

Composition and dissociation constant of the palladium complex in solution

The composition and the dissociation constant of the complexes in solution at 20°–25° were ascertained in the same way as described in a previous paper[1]. For composition, equimolecular solutions of palladium and the reagent were taken in

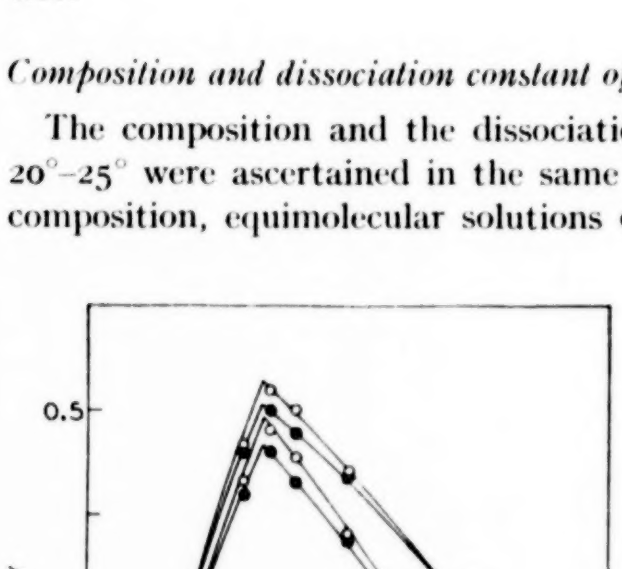

Fig. 5. Mixtures of equimolecular solutions. I 1.88 · $10^{-4}M$, II 0.94 · $10^{-4}M$, III and IV corrected values; (A) 2-Mercaptobenzothiazole; (B) 2-Mercaptobenzimidazole.

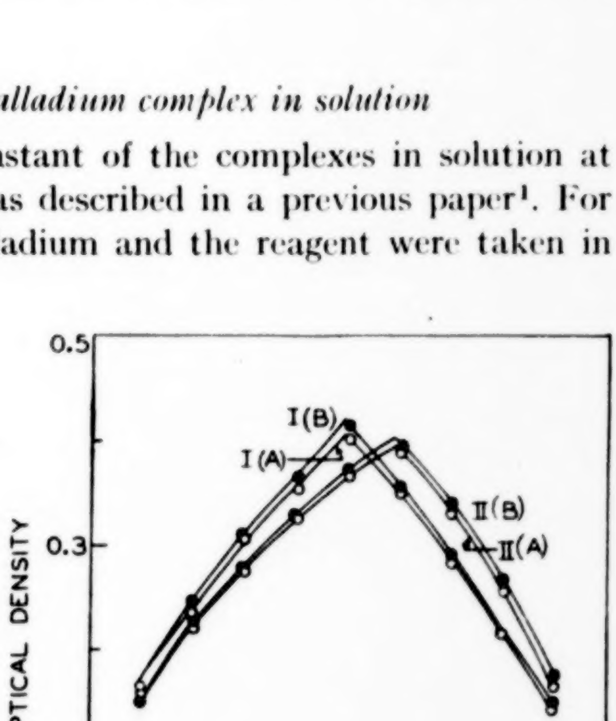

Fig. 6. Mixtures of non-equimolecular solutions. I 0.94 · $10^{-4}M$ Pd and 1.88 · $10^{-4}M$ reagent, II 0.94 · $10^{-4}M$ Pd and 2.82 · $10^{-4}M$ reagent; (A) 2-Mercaptobenzothiazole; (B) 2-Mercaptobenzimidazole.

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different ratios to a constant volume of 20 ml which was then made up to 25 ml with a further addition of 2.5 ml of ethyl alcohol and the same amount of water. The curves in Fig. 5 show that the complexes are formed in the solution when the ratio of palladium to reagent is 1:2.

From the absorption data (Fig. 6) of the mixtures of non-equimolecular solutions at 20°–25°, the dissociation constant 'K' of both complexes has been calculated on the basis of the values of x, p and c, the values of m and n being 1 and 2 respectively (Table IV).

TABLE IV

Curve	*Concn. of Pd* $\times 10^4 M$	*Concn. of reagent* $\times 10^4 M$	x	p	$K \times 10^{12}$
I	0.94	1.88	0.51	2	2.4
II	0.94	2.82	0.41	3	0.4

K (mean) $= 1.4 \cdot 10^{-12}$

SUMMARY

As spectrophotometric reagents for palladium, 2-mercaptobenzothiazole and 2-mercaptobenzimidazole behave more or less in the same way. Colour systems formed by them, at a pH region of 3.0 to 6.5, obey Beer's law at 380 mμ with palladium concentrations of 0.4 to 6.0 μg per ml and the optimum range with the minimum error is from 1.6 to 4.0 μg of palladium per ml at 30.1% and 35.8% transmission with 2-mercaptobenzothiazole and 2-mercaptobenzimidazole respectively. By applying Job's method it was found that in solution the ratio of metal to reagent in the complexes is 1:2, and that the dissociation constants of the complexes are of the order of 10^{-12}.

RÉSUMÉ

Le 2-mercaptobenzothiazole et le 2-mercaptobenzimidazole ont été examinés comme réactifs spectrophotométriques du palladium. La loi de Beer est obéie à 380 mμ pour des concentrations en palladium allant de 0.4 à 6.0 μg/ml.

ZUSAMMENFASSUNG

Es wurde die Anwendungsmöglichkeit von 2-Mercaptobenzothiazol und 2-Mercaptobenzimidazol als Reagenzien zur spektrophotometrischen Bestimmung von Palladium untersucht. Bei 380 mμ gilt das Beer'sche Gesetz für einen Konzentrationsbereich von 0.4 bis 6.0 μg Pd/ml.

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AMPEROMETRIC ESTIMATION OF PALLADIUM

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As early as 1897 SALOMON[1] first proposed the principle of amperometric titration, which in later years has been studied by many other investigators. Because of their sensitive and specific or selective reactions, organic reagents have of late been utilised by several workers as titrants. KOLTHOFF AND LANGER[2] suggested the use of α-nitroso-β-naphthol for the titration of palladium. Of the reagents dimethylglyoxime, salicylaldoxime, oxine and mercaptobenzothiazole, TOMICEK and his co-workers[3] found dimethylglyoxime and mercaptobenzothiazole to be sensitive as well as selective in their reactions with palladium, while WILSON AND WILSON[4] preferred 1,2,3-benzotriazole for its determination.

Mercapto compounds, such as bismuthiol I, bismuthiol II, 2-mercaptobenzothiazole and 2-mercaptobenzimidazole, as reagents for the spectrophotometric determination of palladium have already been described in previous communications[5]. This paper records the findings of the work on the application of the said reagents for the amperometric estimation of that element. Constancy of the diffusion currents in sodium acetate–acetic acid buffer, of palladium and of the reagents enabled us to determine the former element amperometrically.

At an applied potential of —0.3 V (S.C.E.), bismuthiol I was found to be a reliable reagent for the estimation of only 1.2 to 2.5 mg of palladium, whereas with bismuthiol II and 2-mercaptobenzimidazole an applied potential of —0.5 V gives highly satisfactory results with 1.2 to 6.0 mg of the same element. 2-Mercaptobenzothiazole gives a positive error of about 5% when the amount of palladium is 6.0 mg. Further, from the above study it has been observed that the metal forms a 1:1 complex with bismuthiol I, while with the other reagents it forms a 1:2 complex.

EXPERIMENTAL

Apparatus

The amperometric set, consisting of a students' type potentiometer with a range of 0 to 1.6 V of Leeds and Northrup Co., a galvanometer, a micro-ammeter (0 to 30 μA), a titration cell and a saturated calomel electrode, was assembled according to the circuit diagram of LINGANE[6]. The potentiometer was calibrated against a galvanometer used as a null-point detector. The currents were measured at 30° ± 1° with a micro-ammeter whose oscillations were damped with a condenser of 250 μF capacity. The titration cell was connected with a saturated calomel electrode by an agar–potassium chloride bridge.

Solutions

A molar solution of palladium was prepared by proper dilution of a standard palladium chloride solution.

Molar solutions of bismuthiol I (A), bismuthiol II (B), 2-mercaptobenzothiazole (C) and 2-mercaptobenzimidazole (D) were obtained by dissolving separately weighed amounts of the reagents in 50% (v/v) ethyl alcohol.

A sodium acetate–acetic acid buffer solution was prepared by mixing 27.2 g of sodium acetate trihydrate in 11.6 ml of glacial acetic acid (sp.gr. 1.05) and then by diluting the mixture with water to 100 ml.

A 0.2% (w/v) gelatin solution in water and a 15% pyrogallol solution in 50% (v/v) aqueous caustic potash solution were the other solutions used.

Capillary

The characteristics of the capillary used were: m = 1.083 mg/sec, t = 6.0 sec (open circuit in distilled water) and h = 44.9 cm.

Measurements of diffusion currents of palladium and the reagents

A 20 ml portion of the solution of palladium was placed in the titration cell and 5 ml of the sodium acetate–acetic acid buffer solution and 1 ml of the gelatin solution were added. Oxygen-free nitrogen gas of high purity (British Oxygen Co., London) was passed through the alkaline pyrogallol solution and was then bubbled through the solution in the titration cell for 15 min. A few minutes later when the current due to a potential of 0.0 V (S.C.E.) became steady, the mean current which flowed through the micro-ammeter was measured. Afterwards, the steady current for the solution at —0.1 V (S.C.E.) was recorded. Then the voltage was slowly increased to —1.6 V (S.C.E.) and the corresponding steady current was measured. In the same way, diffusion currents for the reagents were measured with 20 ml portions of each solution and the results obtained were plotted in Fig. 1. From the figure, the diffusion currents for palladium and reagents against S.C.E. are: palladium, —0.3 to —0.8 V; bismuthiol I, 0.0 to —0.3 V; bismuthiol II, 0.0 to —0.8 V; 2-mercaptobenzothiazole, —0.4 to —0.6 V; and 2-mercaptobenzimidazole, —0.2 to —0.7 V.

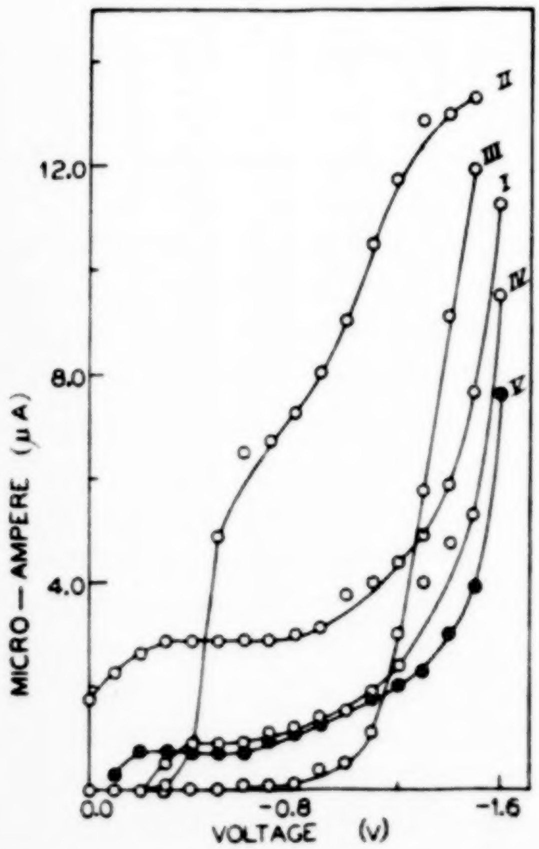

Fig. 1. Diffusion curve. I Palladium ($8.762 \cdot 10^{-4}M$), II Bismuthiol I ($5.318 \cdot 10^{-2}M$), III Bismuthiol II ($2.769 \cdot 10^{-3}M$), IV 2-Mercaptobenzothiazole ($2.663 \cdot 10^{-3}M$), V 2-Mercaptobenzimidazole ($2.8 \cdot 10^{-3}M$).

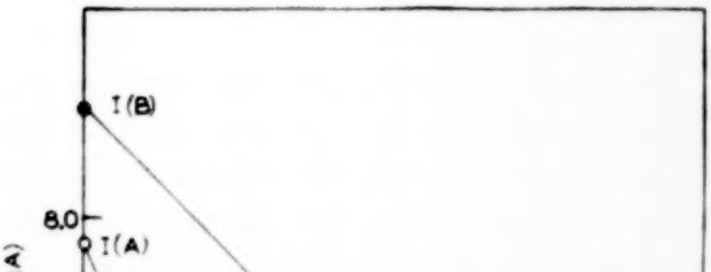

Fig. 2. (A) Bismuthiol I ($5.318 \cdot 10^{-2}M$,) (B) Bismuthiol II ($5.6 \cdot 10^{-2}M$).

Estimation of palladium

An aliquot quantity of the palladium solution was placed in the titration cell along with **5** ml of sodium acetate–acetic acid buffer and 1 ml of gelatin solution. After the addition of water to dilute it to 26 ml, oxygen-free nitrogen gas was passed through the solution for about 15 min. Then when the solution was ready for titration, the tip of a microburette containing the reagent solution was introduced through a hole in the stopper of the titration cell. The circuit was then closed with an applied potential of −0.3 V (S.C.E.) when titrating with bismuthiol I, but with the other reagents as titrants the applied potential was adjusted to −0.5 V (S.C.E.).

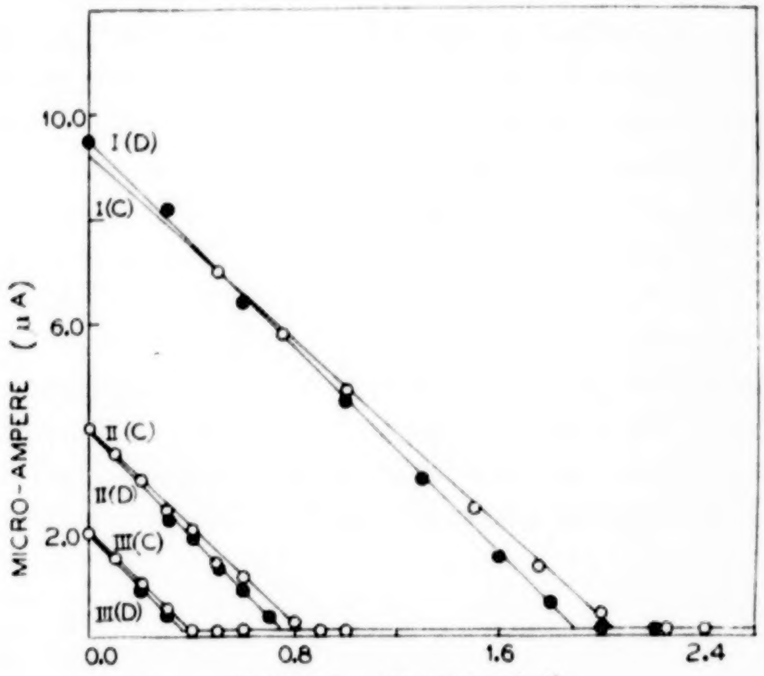

FIG. 3.

Fig. 3. (C) 2-Mercaptobenzothiazole ($5.371 \cdot 10^{-2} M$). (D) 2-Mercaptobenzimidazole ($6.327 \cdot 10^{-2} M$).

When the current became steady, a small quantity of the titrant was run into the cell and after the passage of nitrogen through the solution for one minute, the steady current was measured. On plotting the currents against the volumes of the titrant, the equivalence point was extrapolated. The results are represented in Figs. 2 and 3 and tabulated in Table I.

TABLE I

Curve	*Pd taken mg*	*Pd found (mg)*			*Pd taken mg*	*Pd found mg*
		A	*B*	*C*		*D*
I	6.00	3.80	5.97	6.31	6.50	6.40
II	2.40	2.44	2.39	2.41	2.60	2.55
III	1.20	1.14	1.19	1.20	1.30	1.28

SUMMARY

In sodium acetate–acetic acid buffer the diffusion currents of palladium and of the reagents bismuthiol I, bismuthiol II, 2-mercaptobenzothiazole and 2-mercaptobenzimidazole remain constant respectively at potentials (*vs* S.C.E.) of −0.3 to −0.8 V, 0.0 to −0.3 V, 0.0 to −0.8 V, −0.4 to −0.6 V and −0.2 to −0.7 V respectively. Bismuthiol I, at an applied potential of −0.3 V, is effective for the estimation of 1.2 to 2.5 mg of palladium, whereas bismuthiol II and 2-mercaptobenzimidazole give highly satisfactory results with 1.2 to 6.0 mg of palladium at a potential of —0.5 V. 2-Mercaptobenzothiazole at the latter potential gives an error of about 5% when the concentration of palladium is about 6.0 mg.

RÉSUMÉ

Les auteurs ont effectué une étude en vue d'un dosage ampérométrique du palladium. Les réactifs examinés sont: bismuthiol I, bismuthiol II, 2-mercaptobenzothiazole et 2-mercaptobenzimidazole.

ZUSAMMENFASSUNG

Es wurden die Möglichkeiten einer amperometrischen Bestimmung von Palladium mit Hilfe von Wismutthiol I, Wismutthiol II, 2-Mercaptobenzothiazol und 2-Mercaptobenzimidazol untersucht.

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THE EFFECT OF THE ELECTRONIC STRUCTURE OF THE CATION UPON FLUORESCENCE IN METAL-8-HYDROXYQUINOLINE COMPLEXES

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INTRODUCTION AND THEORETICAL SECTION

Compounds of 8-hydroxyquinoline (oxine) have been prepared with metals in lower valency states in these laboratories[1] in connection with biochemical researches with metallic valency states. The complexes obtained with Mo, V, Fe, Cu, Au and Ti valencies, although distinctly coloured, were non-fluorescent in u.v. light. It is well known that some cations *e.g.* Al^{+3}, Zn^{+2}, Mg^{+2}, Ca^{+2}, Li^{+} etc. will form oxinates which fluoresce brightly in u.v. light, and the fluorescent properties of metallo-oxinates were therefore studied to determine whether a relationship existed between the electronic structure of the cation, and the ability of the complex to fluoresce.

Differences in the fluorescent and phosphorescent lifetimes of some metal–dibenzoylmethane complexes were explained by YUSTER AND WEISSMAN[2] on the basis of varying degrees of interaction between the optical electrons responsible for fluorescence in the complex and the field of the metal ion. This perturbation effect of the ionic field depended considerably upon the protection afforded to the optical electrons by the shells in the ion itself, as complete electron shells afforded more protection than empty shells against perturbation and dissipation of fluorescence. The incomplete 4f shell of the Gd^{+3} ion greatly reduced the luminescent life of the Gd complex owing to the large degree of perturbation caused by the unhomogeneous field of the paramagnetic ion. The non-fluorescence of the Yb^{+3} complex was suggested to be due to the removal of an electron from the 4f^{13} to the 5d or 6s or 6p shell resulting in an "internal quenching" effect.

If the considerations of YUSTER AND WEISSMAN are applied to 8-hydroxyquinoline complexes, it would be expected that the oxinates which fluoresced most readily would be those derived from cations containing the most stable electron groupings, *i.e.* where shells are either full or empty, and that incomplete shells or a transitional nature in the metal ion would reduce or destroy the fluorescence of the oxine complex. In the main this was found to be correct; of the metals which form, or would be expected on account of their electronic structure to form, fluorescent oxinates are shown in Table I.

Oxine compounds of the other metallic elements not listed in Table I were examined with the exception of Tc, Rh, Pm(II), Eu, Ho, Re, Os, Ir, Po and the "uranide" elements, and were found to be non-fluorescent in u.v. light. Those listed which were not examined would be expected on account of their electronic structures to yield non-fluorescent oxinates.

TABLE I

FLUORESCENT METALLO-8-HYDROXYQUINOLATES

Group	*Sub group A*	*Sub group B*
I	Li, Na, K, Rb, Cs, Fr[a]	Ag
II	Be, Mg, Ca, Sr, Ba, Ra[a]	Zn, Cd
III	Al, Sc, Y, La ... (Gd) ... Lu, Ac[a]	Ga, In
IV	Zr, Hf[a], Th	Ge, (Sn), ((Pb))
V	(Nb), Ta, Pa[a]	none
VI	none	none
Uranides	Cm[a]	
VII VIII	none	none

[a] Speculated from electronic structure of ion.
( ) Weak fluorescence.
(( )) Very weak fluorescence.

The alkali metals and Ag, and the alkaline-earth metals, Zn and Cd lose s electrons to form ions of one stable valency in which the remaining electron shells are full. In contrast Cu, Au, and Hg show transitional properties and each possesses two valencies which are relatively stable to one another; a perturbation or internal quenching effect may therefore occur with the optical electrons of their complexes which are consequently non-fluorescent. The behaviour of cations in Group IIIA provides evidence for the weakening of the fluorescent properties of oxinates by the presence of an incomplete 4f shell between La^{+3} and Lu^{+3}. Gd^{+3}, in which the 4f shell is half full (a condition which is regarded as having some stability), gives the weakest fluorescence in the Group. Other members of the rare-earth series in which the 4f shell contains <7, or >7 and <14 electrons yield non-fluorescent oxine complexes[3]. Actinium oxinate would be expected to fluoresce as the electronic groupings in Ac are similar to those in Lu but with 18 electrons added to complete the 5d, 6s and 6p shells. In Group IIIB, Ga and In each possess one stable cation, as ions of the lower valencies are very unstable, but with Tl both the uni- and trivalent cations are reasonably stable giving a transitional character to the metal, and non-fluorescent oxine complexes are formed with both valencies.

The metals in Group IVA show regular behaviour as regards fluorescence. The transitional nature of Ti with its moderately stable tri- and tetravalent states appears to preclude fluorescence in both oxinates derived from these valencies. Zr and Th, which possess only the cationic state M^{+4}, in which the remaining electron shells are full, form fluorescent oxinates, and it is predicted that Hf^{+4}, which like Zr^{+4} is formed by loss of d and s electrons leaving other shells full, will also form a luminescent oxine complex. Unfortunately no Hf material was available at the time this work was carried out.

Group IVB contains the anomalous case of Sn which forms fluorescent compounds with oxine in both Sn^{+2} and Sn^{+4} valency states. It may however be noted that in neither ion is there an incomplete electronic shell; moreover the fluorescence of the Sn compounds is feeble compared with that of the others listed in Table I. The same remarks also apply to Pb; here the fluorescence is very feeble and although the divalent cation is very stable, some stability exists in the Pb^{+4} condition.

In Group VA, as the valencies of less than 5 become increasingly unstable, any perturbing or quenching effects due to transitional character would be expected to become less and hence there is an increasing tendency for the oxinates to fluoresce on passing from V (all oxinates non-fluorescent) via Nb (oxinate of pentavalent state fluoresces feebly) to Ta (pentavalent state gives a moderately bright fluorescent complex). Pa which shows no sign of a valency other than 5, and whose electronic structure is similar to that of Ta but with an added 18 electrons to complete the 5d, 6s, and 6p shells, would be expected to give a fluorescent complex.

In Group VB it may be expected that Bi oxinate would show a feeble fluorescence as Bi^{+3} is the only stable cation in which remaining electron shells are full. However, it does not fluoresce and indeed in other cations which are formed by the loss of p, but not s, electrons from the same shell (*e.g.* Pb, Tl, Sb, Sn and possibly As) the fluorescent properties of the oxine complexes are either feeble or totally absent.

In Groups VI, VII, and VIII, oxinate fluorescence is notably lacking owing possibly to the internal quenching effect which incomplete d electron shells may exert in the highly transitional metals which comprise these Groups.

Of the "uranide elements" of Group VI, it might be expected that a weakly-fluorescent oxinate would be formed by Cm, as this metal has only one valency-state (3), and the electronic structure of the Cm^{+3} ion with its half-complete 5f shell resembles that of Gd^{+3}.

From the observations recorded above, it appears that the possession of fluorescent properties by a metal–8-hydroxyquinoline complex is dependent upon the formation of metal ions of only one stable valency in which the remaining electron shells are in a "symmetrically stable" state, *i.e.* empty, half-full or complete.

The fluorescence intensities, relative to a quinine sulphate standard, of a number of pure metal oxinates of the type $M(C_9H_6ON)_n$, where n = the valency of the metal ion, M, were examined by measuring the total fluorescent light emitted after irradiation of chloroform–ethanol solutions of the complexes with u.v. light. Concentrations of each complex from $\frac{M}{500}$ to $\frac{M}{10^6}$ were tested, and in dilute solutions $\left(\frac{M}{10^6} \text{ or } \frac{M}{10^5}\right)$ the fluorescent intensities of the compounds decreased in the series:

$$\text{Al} > \text{Y} > \text{Sc, Zr, Mg, Sn} > \text{Be} > \text{Zn} > \text{Ag} > \text{Li} > \text{Na}$$

The series was gradually broken up in solutions containing an increasing concentration of metal oxinate. Although these results do not provide much that is conclusive, it is interesting to note that as with the dibenzoylmethane complexes of YUSTER AND WEISSMAN[2], the Al compound exhibits the greatest degree of fluorescence, followed by Y and Sc. The weaker fluorescence of Ag may be due to some decomposition within the complex, and the relatively poor response of Li and Na is possibly because of a greater tendency to dissociate in the solvent.

The position of Sn in the series is anomalous, but a very pronounced quenching of the fluorescence of a Sn^{+2} oxinate solution takes place with increasing concentration. Thus the intensities at $\frac{M}{10^5}$, $\frac{M}{10^4}$ and $\frac{M}{10^3}$ are respectively 32%, 21% and 1% (based on the quinine sulphate standard). This is presumably due to the ready dissipation of the excitation energy in the molecules by collisions.

EXPERIMENTAL SECTION

Preparation of 8-hydroxyquinoline complexes

Most of the complexes were prepared in the standard way, using AnalaR materials, by mixing an aqueous-ethanolic solution of a suitable salt with an ethanolic solution of oxine, and precipitating the oxinates by the gradual addition of NH_4OH to the solution. The precipitates were filtered by suction, washed with water, ethanol, and ether and dried at the correct temperature. The preparation of oxine compounds which did not appear to have been previously reported, or which needed modified techniques are described below. Where necessary, the compositions of the compounds prepared were checked by C, H, N and, where appropriate, Cl analyses.

The alkali metals

Two methods were used for this group: (1) A "wet" method in which oxine was dissolved in a hot solution of the hydroxide; on cooling the precipitated complex was dried by suction filtration, dissolved in a minimum of warm ethanol and re-precipitated by the addition of an excess of ether. This precipitate was filtered off and washed with ether and dried at 90°. (2) A "dry" method where 1 part by weight of the anhydrous metal carbonate was added to 4–5 parts of molten oxine, and the temperature raised to boiling point. When the carbonate had dissolved according to the suggested reaction $M_2CO_3 + 2C_9H_7ON \rightarrow 2M(C_9H_6ON) + H_2O + CO_2$ the melt was cooled and powdered and dissolved in either hot 95% acetone (Li, Na, K) or hot ethanol (Rb, Cs). From the cooled solutions, after filtration (No. 41 filter paper), the oxinates were precipitated by adding an excess of ether. They were filtered by suction, washed with ether and dried.

The reaction between carbonates and molten oxine did not appear to be confined to the metals of Group IA, as the carbonates of Ag, Cu and Pb reacted in a similar way. Ca, Ba, and Bi carbonates in contrast appeared to remain unaffected by boiling oxine.

The Rb and Cs compounds, which do not appear to have been previously reported, were difficult to prepare by the "wet" method because they would not crystallise from the hydroxide solutions, due possibly to a higher degree of dissociation than with the K and Na complexes.

It would be expected that the power of the N atom of 8-hydroxyquinoline to co-ordinate with an alkali metal becomes less on passing from Li to Cs, and in conjunction with the weakly acidic H atom of the OH group it is not surprising that the Rb and Cs compounds approached the composition $MOH \cdot C_9H_7ON$ as indicated by the analyses below:

Found, for Rb: C 42.3, H 4.0, N 5.3. (Calc. for $RbOH \cdot C_9H_7ON$, C 43.7, H 3.2, N 5.6).
Found for Cs: C 35.6, H 2.8, N 4.6. (Calc. for $CsOH \cdot C_9H_7ON$, C 36.6, H 2.7, N 4.7).

The alkali metal oxinates were soluble in water (Li sparingly) and ethanol but insoluble in ether and chloroform. When the K, Rb, or Cs compounds were treated with a chloroform–acetone mixture (3:1) and warmed, a green or blue colour was produced at first and finally a purple solid was deposited. With K oxinate prepared by the "wet" method (and probably containing a little free alkali) the mixture boiled without any previous heating; the resulting purple solid was washed with ether and dried in vacuo over P_2O_5 in a desiccator. The purple compound contained Cl and was stable in air; it was however decomposed by warming, and also by water, which yielded an ink-blue solution. When the blue solution was boiled or the purple compound heated oxine vapour, but no chloroform, was evolved. The compound did not fluoresce in u.v. light and analyses showed that it was of variable composition. It is of interest to note that previous workers have observed a green or blue colour during the reaction of $CHCl_3$ and CCl_4 with hydroxyquinolines or β-naphthol respectively in caustic alkali solution[4,5].

The readiness to form this purple compound decreased from K *via* Na, where a slow reaction took place, to Li whose oxinate reacts only slightly. Oxinates prepared by the "wet" method reacted much more readily with chloroform than those produced by the "dry" method, owing possibly to the presence of a little free alkali in the former.

It was also noted that a blue-green colour was produced by the action of chloroform upon the oxine compounds of some alkaline earth metals and here again colour production decreased with decreasing basicity of the metal ion. The Ba compound gave considerable colour, at Ca it was slight, and no action appeared to take place with the Mg and Be complexes.

The action of carbon tetrachloride, methylene and ethylene dichlorides upon K oxinate was found to be slight; trichloroethylene and ethyl iodide were without effect.

Sc and Nb

The oxinates were prepared from Johnson-Matthey "specpure" Sc_2O_3 and B.D.H.

Nb_2O_5 respectively. Fusion with sodium bisulphate was necessary to obtain the elements in soluble form. After cooling, the melts were powdered and extracted with hot water. Sc was precipitated with ammonia, and the $Sc(OH)_3$ was filtered, washed and re-dissolved in warm dilute sulphuric acid. The Nb melt was hydrolysed during hot water treatment, and the precipitated Nb_2O_5 was filtered off and washed, and dissolved in warm concentrated sulphuric acid. The H_2SO_4 solution was cooled in ice water and diluted with acetone. The Sc and Nb oxine compounds were then prepared from these solutions in the standard way.

Sn

The oxine complexes of Sn do not seem to have been extensively studied. When solutions of $SnCl_2$ in HCl and oxine in ethanol were mixed, a yellow granular compound, which contained Cl, was precipitated. Analyses suggested that the compound was of variable composition.

When ethanol and water were added to the vessel in which this compound was precipitated, and the mixture heated, the precipitate dissolved. Addition of ammonia to the hot solution caused precipitation of a yellow solid, containing no Cl. Found: C 53.4, H 3.3, N 7.1. Calc. for $Sn(C_9H_6ON)_2$, C 53.2, H 3.0, N 6.9. This complex which, unlike the Cl-containing one, was easily soluble in chloroform was used in the measurement of fluorescence intensities (see below). Both compounds when decomposed with HCl formed solutions which readily reduced $HgCl_2$, due to the liberation of Sn^{+2} ions.

Compounds precipitated from solutions of $SnCl_4$ by oxine were also yellow and of variable composition. They would not dissolve in excess of hot aqueous ethanol or in chloroform and yielded non-reducing solutions when decomposed with HCl.

Ge

The only oxine complex of this metal which, to the author's knowledge, has been prepared is a molybdo-oxine compound to which the formula $(C_9H_7ON)_4H_4[Ge(Mo_{12}O_{40})]$ was assigned[6]. LEDERER reported the fluorescence of Ge spots on chromatograms developed with 8-hydroxyquinoline[7]. A yellow fluorescent powder was prepared by treating an ethanolic solution of $GeCl_4$ (prepared by boiling GeO_2 with 7–10*N* HCl and diluting the distillate with ethanol) with ethanolic oxine. Ammonia was added until the pH of the mixture was 4–5, and the volume of the solution reduced by boiling in a stream of CO_2 until on cooling in ice-water a granular precipitate separated out. This was filtered off and washed with water and ether and dried overnight in vacuo over P_2O_5. The yellow powder contained no Cl and was readily soluble in chloroform. When heated, decomposition began at about 110°, and was very marked at 150°. Analysis of the compound gave C 54.8, H 4.3, N 7.2. (Calc. for $(HO)_2Ge(C_9H_6ON)_2$, C 54.7, H 3.6, N 7.1).

Ta

SZYMANSKI AND ARCHIBALD[8] reported the preparation of an orange Ta-oxine compound, to which they assigned the formula $Ta(C_9H_6ON)_5 \cdot 5HCl$, by adding a solution of oxine in benzene to one of $TaCl_5$ in the same solvent. The author found

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that this compound would not fluoresce in u.v. light, but if the solutions were mixed in the reverse order, a pale yellow precipitate was formed which fluoresced brightly in u.v. light. A fluorescent powder was also produced by passing oxine vapour, carried by dry CO_2, over heated $TaCl_5$ in a combustion tube.

An oxine compound of Ta, which appeared to be of constant composition, was prepared by fusing $TaCl_5$ (0.3 g) with oxine (6 g) and heating the mixture just to boiling point. The red liquid was cooled, and the resulting orange solid powdered and dissolved in the minimum quantity of warm ethanol. To this solution, after filtration, excess of ether was added and the mixture allowed to stand for about 30 min to let the precipitate flocculate. The latter was then filtered off and washed with ether, and dried over P_2O_5 in vacuo. The resulting yellow powder fluoresced greenish-yellow in u.v. light and was soluble in a mixture of chloroform and ethanol (9:1) giving a clear yellow solution. Analysis of the compound gave, on two independently prepared samples: C 58.8 H 4.7 N 7.7 Cl 18.9

58.8 4.7 8.0 20.2.

This compound could not be SZYMANSKI AND ARCHIBALD's complex which would have the composition C 50.0, H 3.2, N 6.4, and Cl 16.3. Recrystallisation of the orange powder, obtained by cooling the $TaCl_5$–oxine melt, from ethanol gave a red non-fluorescent compound of the composition C 60.8, H 4.7, N 7.7, Cl 9.45.

Comparison of fluorescence intensities

Stock solutions of the oxinates in chloroform–ethanol (1:1) were prepared by dissolving the correct weight of each complex in the solvent and diluting to volume. The strengths of the stock solutions were $\frac{M}{500}$ for Li, Na, Be, Zn, Al and Zr, $\frac{M}{1000}$ for Sn, $\frac{M}{4000}$ for Y, $\frac{M}{5000}$ for Ag and Mg and $\frac{M}{10^4}$ for Sc. Dilutions were made with

TABLE II

Oxinate of:	*Mol. wt.*	*% Fluorescence of solution* $\frac{M}{10^6}$	$\frac{M}{10^5}$
Al	459	18.6	128.2
Y	521	i.s.	51·5
Sc	622	,,	34·5
Zr	667	,,	34·5
Mg	312	,,	34·0
Sn^{+2}	406	,,	32.0
Be	297	,,	22.4
Zn	353·5	,,	10.6
Ag[a]	397[a]	,,	5·5
Li	151	,,	i.s.
Na	167	,,	,,

i.s. = insignificantly small *i.e.* where total fluorescence is <5%.

[a] $AgC_9H_6ON \cdot C_9H_7ON$.

the solvent as required. Measurements were made on the solutions using the fluorimeter attachment (SP 550) for the Unicam SP 500 Spectrophotometer (silica cells). Readings were taken using the red and blue photocells, first on the solvent and then on the oxinate solutions, and combining the differences to give total fluorescence. This was expressed as a percentage of the light emitted by the quinine sulphate standard (2.5 p.p.m. in 0.1 N H_2SO_4) for which the instrument was set to read 100% fluorescence.

Chloroform–ethanol was used as the solvent because in pure chloroform the initial clear solution of Zn oxinate soon became turbid, and in which also the alkali metal compounds would not dissolve. The values of some relative fluorescence intensities (total) are given in Table II.

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SUMMARY

Experimental evidence suggests that the existence of only one stable cationic valency-state, in which the remaining electron shells are empty, half-full or complete are necessary conditions for the fluorescence of a metal–8-hydroxyquinoline complex in u.v. light. The preparations of hitherto unreported compounds of 8-hydroxyquinoline with Rb, Cs, Ge, Sn and Ta are described.

RÉSUMÉ

L'auteur a examiné les complexes métalliques de l'hydroxy-8-quinoléine et l'effet de la structure électronique du cation sur la fluorescence en lumière ultra-violette. La préparation de certains de ces composés est décrite.

ZUSAMMENFASSUNG

Es wird nachgewiesen, dass bei den Metall-Komplexen des 8-Oxychinolins die Elektronen-Konfiguration des Kations ausschlaggebend für das Auftreten von Fluoreszenz im U.V.-Licht ist. Die Darstellung einer Reihe von neuen Metallverbindungen des 8-Oxychinolins wird beschrieben.

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HALF-WAVE POTENTIALS OF METAL IONS IN ORGANIC HYDROXYACID SUPPORTING ELECTROLYTES. II

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INTRODUCTION

The first paper of this series[1] tabulated the polarographic characteristics of a number of metal ions in eight supporting electrolytes containing citrate, malonate, and tartrate ions. This paper presents similar data for ammoniacal solutions of the ammonium salts of these ions and for ammoniacal ammonium oxalate; to fill a gap in the literature, data are also included for a weakly acidic citrate medium. Data for a few metal ions in ammoniacal citrate, oxalate, and tartrate have been published by LINGANE[2] and MEITES[3], while isolated data in weakly acidic citrate media have been reported by HAMM, SHULL AND GRANT[4], HARRIS[5], HEYROVSKY[6] and KALOUSEK[6,7], LINGANE[2,8] and MEITES[8,9], NEUMAN, HAVILL AND FELDMAN[10], NORTON, STOENNER AND MEDALIA[11] and VANDENBOSCH[12], and a more complete study in such a medium has been described by DONO, MORINAGA AND NOMURA[13].

EXPERIMENTAL

The supporting electrolyte solutions were prepared by mixing the calculated amounts of reagent-grade ammonia and the appropriate acid. All pH values were measured with a Beckman Model G glass electrode pH meter, using saturated potassium hydrogen tartrate[14,15] as the reference standard.

The stock metal ion solutions were prepared from the best available salts. These were diluted so that the concentration of metal ion in the solution examined polarographically was always very nearly 1.0 m*M*, except in the case of thallous ion, whose concentration was always 0.2 m*M*. No maximum suppressor was used except as noted in the Tables.

All measurements were made at 25.00°, using the polarographic apparatus described in the second paragraph of the EXPERIMENTAL section of the preceding paper[1]. The solutions were deaerated with prepurified nitrogen; special care was taken to prevent the air-oxidation of such easily oxidizable species as those formed from iron(II), tin(II), and vanadium(IV). Drop times were generally between 2.5 and 4 sec.

Some of the data were secured with a silver – silver chloride – saturated potassium chloride reference electrode, but all half-wave potentials are referred to the saturated calomel electrode.

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The symbols employed in the following Tables were defined in the preceding paper.

TABLE I

HALF-WAVE POTENTIALS IN 0.1 *F* AMMONIUM CITRATE, pH 6.1

Element and oxidation state	$E_{1/2}$, *V vs. S.C.E.*	*Oxidation state of product*	$E_{3/4}-E_{1/4}$, *mV*	*Notes**
Ag(I)	>0	0		Very i.-d., AgCl ppts.
As(III)	—1.456	—III	—152	I.-d., very large max.
As(V)	NR			
Bi(III)	—0.313	0	— 25	W.-d., very large max.
Cd(II)	—0.700	0	— 28	Very w.-d.
Co(II)	NR			
Cr(III)	—1.151	II(?)	—108	Abnormally small, not w.-d.
Cr(VI)	>0	III + VI		$i = 3/4 i_{total}$.
	—0.383	III	— 55	W.-d.
Cu(II)	—0.170	0	— 23	W.-d., small max. Reaction definitely does not produce Cu(I).[7]
Fe(II)	(—0.183)	III	+ 57	W.-d.
Fe(III)	—0.225	II	— 75	W.-d.
In(III)	NR			
Mn(II)	—1.615	0	— 52	I.-d.
Mo(VI)	—1.011		—130	Very w.-d. Wave height is close to expected value for $n = 3$.[9]
Ni(II)	NR			
Pb(II)	—0.542	0	— 27	W.-d., very small max.
Sb(III)	—0.771		— 54	Very w.-d., $i = 1/4\ i_{total}$.
	—1.120		—109	Very w.-d., $i = 3/7\ i_{total}$.
	—1.50	0		I.-d. Presumably 3 complexes in sluggish equilibrium.
Sb(V)	—1.564	0(?)	— 76	I.-d., wave height only about 2/3 of expected value for $n = 5$.
Sn(II)	(—0.406)	IV	+ 36	W.-d.
	—0.662	0	— 38	W.-d.
Sn(IV)	—1.0			Some indication of a very small wave.
Te(VI)	—1.237	—II	— 73	Very w.-d.
Tl(I)	—0.510	0	— 28	W.-d.
U(VI)	—0.415	IV + V	— 35	Max. at top of wave, min. at —0.9 V.
V(IV)	—0.44			Some indication of a very small wave.
	—1.485	II	—121	I.-d.
V(V)	>0	IV		W.-d., large max.
	—1.532	II	—190	I.-d.
W(VI)	—1.497	H_2(?)		Very i.-d., wave height corresponds to $n = ca.\ 5$.
Yb(III)	NR			
Zn(II)	—1.373	0	—165	I.-d.

* i.-d. = ill-defined; w.-d. = well-defined.

TABLE II

HALF-WAVE POTENTIALS IN 0.1 *F* AMMONIA–0.1 *F* AMMONIUM CITRATE, pH 8.5

Element and oxidation state	$E_{1/2}$, *V vs. S.C.E.*	*Oxidation state of product*	$E_{3/4}-E_{1/4}$, *mV*	*Notes*
Ag(I)	>0	0		W.-d., large rounded max.
As(III)	-1.62_9	—III	— 57	Fairly w.-d., max.
As(V)	NR			
Bi(III)	—0.435	0	— 45	W.-d., rounded max. at 1.3 V.
Cd(II)	—0.706	0	— 42	Very w.-d.
Ce(IV)	>0	III		Very w.-d.
Co(II)	-1.38_7	0	— 82	Fairly w.-d.
	—1.7			Some indication of a small wave.
Cr(III)[a]	NR			
Cr(VI)	—0.235	III	— 75	Very w.-d. to *ca.* —0.9 V, then rises gradually.
	—1.8	0		Very i.-d.
Cu(II)	—0.165	I	— 58	Fairly i.-d.
	—0.340	0	— 58	Very w.-d.
Fe(II)	(—0.438)	III	+ 35	W.-d., max.
	—1.63	0		Very i.-d., height only about 1.5 times that of anodic wave.
Fe(III)	—0.457	II	— 58	Very w.-d., $i = 1/3\ i_{total}$.
	—0.935			W.-d., $i = 1/6\ i_{total}$.
	—1.61	0		I.-d., $i = 1/2\ i_{total}$.
In(III)	-1.34_6	?	—145	I.-d. and abnormally small.
Mn(II)	-1.62_4	0	— 71	I.-d.
Mo(VI)	-1.25_7	V	—122	Fairly w.-d., $i = 1/2\ i_{total}$.
	—1.70	IV		I.-d.
Ni(II)	-1.09_3		— 82	I.-d.
	-1.39_5	0	—106	Fairly w.-d. Probably two complexes in sluggish equilibrium.
Pb(II)	—0.522	0		W.-d., acute max.
Pb(II)[b]	—0.528	0	— 28	W.-d.
Sb(III)	—0.972	0	—114	Very w.-d.
	—1.79	—III		Very i.-d., max.
Sb(V)	NR			
Sn(II)	(—0.470)	IV	+ 13	W.-d. but oscillations are abnormally large near foot of wave.
	—0.752	0	— 57	Very w.-d. Curves change slightly with time; these data are for solutions aged to apparent equilibrium (*ca.* 30 min).
Sn(IV)	NR			
Te(VI)	—1.296	—II	— 73	Very w.-d.
Tl(I)	—0.447	0	— 58	W.-d.
U(VI)	—0.585	V	— 49	I.-d., max., wave height only about half expected value for $n = 1$.
	—1.065	IV	—132	Very w.-d., total wave height agrees with expected value for $n = 2$.
V(IV)	(—0.05)	V		Very i.-d.
	-1.48_2	II	—170	Fairly w.-d.

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(Contd. on p. 400)

TABLE II (Continued)

Element and oxidation state	*$E_{1/2}$, V vs. S.C.E.*	*Oxidation state of product*	*$E_{3/4}$—$E_{1/4}$, mV*	*Notes*
V(V)	—0.268	IV	— 51	I.-d., large rounded min at *ca.* —0.75 V.
	—1.358	II	—101	W.-d.
W(VI)	—1.59	H_2(?)	— 53	I.-d., large max., wave height corresponds to n = *ca.* 12.
Yb(III)	NR			
Zn(II)[b]	—1.236	0	— 50	W.-d.

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[a] Extensive precipitation from a 1 m*M* solution.

[b] With 0.002% Triton X-100.

TABLE III

HALF-WAVE POTENTIALS IN 0.1 *F* AMMONIA–0.1 *F* AMMONIUM MALONATE

Element and oxidation state	*$E_{1/2}$, V vs. S.C.E.*	*Oxidation state of product*	*$E_{3/4}$—$E_{1/4}$, mV*	*Notes*
Ag(I)	>0	0		Max. at ± 0.0 V is suppressed by 0.002% Triton X-100.
As(III)	—1.633	—III	— 82	I.-d., max. at —1.7 V is suppressed by 0.005% gelatin but not by 0.002% Triton X-100.
As(V)	NR			
Bi(III)[a]	NR			
Cd(II)	—0.676	0	— 28	W.-d.
Ce(IV)[a]	NR			Brownish-white ppt.
Co(II)	—1.217	0	— 49	W.-d.
Cr(III)[a]	NR			
Cr(VI)	—0.189[b]	III	— 68	Incompletely suppressed max. at —0.32 V is followed by long min. after which plateau assumes the normal shape.
	—1.701[c]	0	— 61	Max. at —1.71 V suppressed by gelatin.
Cu(II)[d]	—0.096	I	— 46	I.-d.
	—0.307	0	— 60	W.-d., max. at —0.54 V is suppressed by Triton.
Fe(II)	(—0.282)	III	+ 51	W.-d.
	—1.434	0	— 32	W.-d.
Fe(III)[a]	NR			
In(III)[a]	NR			
Mn(II)	—1.535	0	— 35	W.-d.
Mo(VI)[c]	—1.667	?	— 52	W.-d., max. at —1.80 V suppressed neither by gelatin nor by 0.002% Triton X-100. Wave height corresponds to n = *ca.* 3 without gelatin, *ca.* 8 with gelatin.
Ni(II)[b]	—0.983	0	— 75	W.-d., max. at —1.20 V is suppressed by Triton.
Pb(II)	—0.457	0	— 30	W.-d., some pptn. from a 1 m*M* solution.
Sb(III)	—0.670	0	—111	W.-d., small max. at —0.68 V is not suppressed by 0.002% Triton X-100.

(Contd. on p. 401)

TABLE III (Continued)

Element and oxidation state	*$E_{1/2}$, V vs. S.C.E.*	*Oxidation state of product*	*$E_{3/4}-E_{1/4}$, mV*	*Notes*
Sb(V)	NR			
Sn(IV)	NR			
Te(VI)[c]	-1.291	$-$II	-107	W.-d., max. at -1.34 V is suppressed by gelatin.
Tl(I)	-0.464	0	-52	W.-d.
U(VI)	-0.509	V(?)	-66	W.-d., some pptn. from a 1 m*M* solution.
V(IV)	(-0.249)	V	$+36$	I.-d.
	(-0.460)			Small anodic prewave.
	-1.324	II	-82	I.-d.
V(V)	-0.39			Small cathodic prewave.
	-1.02_7	IV	-116	I.-d.
	-1.28_6	II	-98	I.-d.
W(VI)[c]	-1.59_0	H_2(?)	-83	I.-d., max. at -1.69 V not suppressed by gelatin. Wave height corresponds to $n =$ *ca.* 15 without gelatin, *ca.* 10 with gelatin.
Yb(III)	-1.71_9	II	-89	I.-d.
Zn(II)	-1.138	0	-48	W.-d.

[a] Extensive precipitation from a 1 m*M* solution.
[b] With 0.002% Triton X-100.
[c] With 0.005% gelatin.
[d] With 0.005% Triton X-100.

TABLE IV

HALF-WAVE POTENTIALS IN 0.1 *F* AMMONIA–0.1 *F* AMMONIUM OXALATE

Element and oxidation state	*$E_{1/2}$, V vs. S.C.E.*	*Oxidation state of product*	*$E_{3/4}-E_{1/4}$, mV*	*Notes*
Ag(I)	>0	0		Very w.-d., large max. at -0.04 V is suppressed by 0.004% Triton X-100.
As(III)	-1.7	$-$III		Max., plateau has fairly large positive slope.
As(V)	NR			
Bi(III)[a]	-0.36			
Cd(II)	-0.705	0	-57	Very w.-d.
Ce(IV)[a]	NR			Yellow precipitate.
Co(II)	-1.314	0	-81	Very w.-d.
Cr(III)	-1.64	0		Small i.-d. irreversible wave, partial pptn.
Cr(VI)	-0.237	III	-55	Very w.-d., small max.
	-1.7	0		Sharp max. followed by sharp min., then by plateau having positive slope.
Cr(VI)[b]	-0.284			Fairly i.-d.
	-1.15	III	-180	$i_2 = 2i_1$; total height same as that of first wave without Triton.
	-1.68	0		I.-d., max. and min. suppressed by Triton.
Cu(II)	-0.176	I	-50	W.-d.
	-0.379	0	-62	Very w.-d., small rounded max. at -0.7 V.
Cu(II)[b]	-0.172	I	-50	W.-d.
	-0.407	0	-95	Max. suppressed by Triton.

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(Contd. on p. 402)

TABLE IV (Continued)

Element and oxidation state	*$E_{1/2}$, V vs. S.C.E.*	*Oxidation state of product*	*$E_{3/4}-E_{1/4}$, mV*	*Notes*
Fe(II)	(—0.287)	III	+ 57	W.-d.
	—1.518	0	— 50	W.-d., small rounded max. at —1.6 V.
Fe(II)[b]	(—0.286)	III	+ 59	W.-d.
	—1.560	0	— 68	W.-d., max. suppressed by Triton.
Fe(III)[a]	NR			
In(III)	—0.906	?	—117	Abnormally small wave, no pptn.
Mn(II)	—1.599	0	— 37	Fairly w.-d.
Mo(VI)	—1.66_3	?	— 53	Very i.-d.
Ni(II)	—1.073	0	— 97	Fairly w.-d.
Pb(II)	—0.532	0	— 25	Very w.-d.
Sb(III)	(—0.2)	V		Some indication of a very i.-d. anodic wave.
	—0.792		— 29	Presumably two complexes in sluggish equilibrium;
	—0.899	0	— 34	$i_3 = 1/4\ i_2$.
	—1.7	—III		Very i.-d., max.
Sb(III)[b]	(—0.2)	V		Some indication of a very i.-d. anodic wave.
	—0.800		— 30	Very w.-d.
	—0.926	0	— 61	Very w.-d., $i_3 = 1/2\ i_2$.
	—1.8	—III		Max. suppressed by Triton.
Sb(V)	NR			
Sb(II)	—1.12		— 47	Small prewave.
	—1.465	0	— 65	Fairly w.-d., small max.
Sn(II)[b]	—1.4			Prewave, height decreased 50% and max. suppressed by Triton.
	—1.540	0	—170	Very i.-d.
Sn(IV)	—1.510	0(?)	— 51	I.-d., $i = 1/4\ i_{total}$.
	—1.74_8		— 76	I.-d., total wave height is 3 times expected value for $n = 4$.
Te(IV)	—0.704	0	— 58	Very w.-d. to huge max. at —1.2 V, i.-d. thereafter.
Te(IV)[b]	—0.755	0	— 62	W.-d., max. reduced by Triton.
Te(VI)	—1.337	—II	— 71	Very w.-d., max. on rising portion of wave.
Te(VI)[b]	—1.408	—II	— 91	Very w.-d., max. suppressed by Triton.
Ti(III)[a]	NR			
Tl(I)	—0.473	0	— 59	Very w.-d.
U(VI)	—0.498	V	— 63	Very w.-d. to —1.0 V, oscillations irregular thereafter.
V(IV)	(—0.272)	V	+ 89	
	—0.99			Small cathodic prewave.
	—1.318	II	— 74	Very w.-d.
V(IV)[b]	(—0.214)	V	+ 69	
	—1.09			Small cathodic prewave.
	—1.403	II	— 86	Very w.-d.
W(VI)	—1.62_6	H_2(?)	— 54	Fairly i.-d., large max.
Yb(III)	NR			
Zn(II)	—1.229	0	— 25	Very w.-d., max.
Zn(II)[b]	—1.243	0	— 45	Very w.-d., max. suppressed by Triton.

[a] Extensive precipitation from a 1 m*M* solution. [b] With 0.004% Triton X-100.

TABLE V

HALF-WAVE POTENTIALS IN 0.1 *F* AMMONIA–0.1 *F* AMMONIUM TARTRATE

Element and oxidation state	*$E_{1/2}$, V vs. S.C.E.*	*$i_d/C\, m^{2/3}t^{1/6}$, µA/mmole/l/mg$^{2/3}$sec$^{-1/2}$*	*Oxidation state of product*	*$E_{3/4}$—$E_{1/4}$, mV*	*Notes*
Ag(I)	>0				Max. at 0.0 V.
As(III)	—1.570	22.8	—III	— 71	Very i.-d., max. at —1.73 V nearly eliminated by 0.002% Triton X-100.
As(V)	NR				
Bi(III)	—0.543	4.23	0	— 66	Very w.-d.
Cd(II)	—0.727	3.40	0	— 36	Very w.-d.
Ce(IV)	—0.172	1.18	III	—172	Suggests two poorly separated waves.
	—1.015	1.74		—300	Possibly anomalous.
Co(II)[a]	—1.225	1.88	0	— 43	W.-d., small max. eliminated by Triton.
Cr(III)[b]	NR				
Cr(VI)	—0.244	6.23	III	— 43	Max. at —0.35 V, w.-d. to —1.3 V, i.-d. thereafter. Polarogram deformed by 0.005% Triton X-100.
Cu(II)[a]	—0.147	1.9	I	— 61	Fairly i.-d.
	—0.382	4.1	0	— 77	Max. at —0.57 V. eliminated by Triton, very w.-d.
Fe(II)	(—0.469)	—1.11	III	+118	Max. at —0.3 V, very w.-d., min. at 0.0 V.
	—1.418	+0.93	0	— 37	Very w.-d.
Fe(III)	—0.829	1.25	II	—144	I.-d.
	—1.416	3.94	0	— 28	Very w.-d.
In(III)	—1.156	1.28	?	—150	W.-d.
Mn(II)	—1.528	2.10	0	— 35	Very w.-d.
Mo(VI)	NR				
Ni(II)[a]	—0.960	3.16	0	— 52	Very w.-d., max. suppressed by Triton.
Os(VIII)	—0.259	1.5	VI	— 34	W.-d.
	—1.509	68	H_2	— 94	I.-d.
Pb(II)[a]	—0.541	2.67	0	— 26	Very w.-d., max. suppressed by Triton.
Ru(IV)	—1.577	17	H_2	— 74	
Sb(III)[a]	—0.952	3.74	0	—107	I.-d.
Sb(V)[c]	—1.715		?	— 64	I.-d.
Sn(II)[a]	(—0.534)	—2.54	IV	+ 42	Very w.-d.
	—0.769	+3.02	0	— 22	Very w.-d., max. suppressed by Triton.
Sn(IV)	NR				
Te(IV)	—0.705	6.39	0	— 74	W.-d. to huge max. at —1.26 V, i.-d. thereafter.
Te(VI)[a]	—1.513	10.1	—II	—123	I.-d., max. nearly suppressed by Triton.
Tl(I)	—0.468	2.21	0	— 57	Very w.-d.
U(VI)	—0.661	1.52	V	— 38	W.-d.
	—1.08	2.54	IV	—180	I.-d.
V(IV)	(—0.212)	—0.95	V	+ 68	Very i.-d.
	—1.576	1.17	III	— 92	Very i.-d.
V(V)	—0.26				Prewave with broad min. at —0.65 V.
	—0.979	1.58	IV	—190	Fairly w.-d.
	—1.58	3.2	III	—160	Very i.-d.

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TABLE V (Continued)

Element and oxidation state	*$E_{1/2}$, V vs. S.C.E.*	*$i_d/C\,m^{2/3}t^{1/6}$, μA/mmole/l/mg$^{2/3}$sec$^{-1/2}$*	*Oxidation state of product*	*$E_{3/4}-E_{1/4}$, mV*	*Notes*
W(VI)	−1.627	20.3	H_2	−33	I.-d.
Yb(III)	NR				
Zn(II)[a]	−1.204	3.32	0	−40	W.-d., max. suppressed by Triton.

[a] With 0.001% Triton X-100.

[b] Apparently quantitative precipitation from a 1 m*M* solution.

[c] Partial precipitation from a 1 m*M* solution.

SUMMARY

Information is presented on the half-wave potentials, reversibilities, wave shapes, and probable electrode reaction products for the polarographic waves of most of the common heavy metal ions in 0.1 *F* ammonium citrate at pH 6 and in 0.1 *F* ammonium citrate, malonate, oxalate, and tartrate containing 0.1 *F* ammonia.

RÉSUMÉ

Les auteurs ont étudié le comportement polarographique de la plupart des ions métalliques courants en présence de différentes solutions de base.

ZUSAMMENFASSUNG

Es wird das polarographische Verhalten der am meisten vorkommenden Schwermetall-Ionen in ammoniakhaltigen Lösungen von Ammonium-citrat, -malonat, -oxalat und -tartrat beschrieben.

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HIGH PRECISION TITRIMETRY*

II. A SYSTEM OF WEIGHT TITRIMETRIC ANALYSIS USING ARBITRARY STANDARDS

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An examination of the mechanical precision of normal titrimetric operations[1], and comparison with practical precision has lent support to the idea that there exists a limiting precision, and therefore accuracy, for analytical processes beyond which improvement in mechanical precision gives no improvement in results. Further to establish this point, methods are suggested for increasing mechanical precision of measurement to the limit, and used to investigate precision and accuracy of certain determinations at a degree of mechanical precision beyond the inherent errors of chemical reaction and location of end-point.

Fully to realise the best precision of which ordinary volumetric methods are capable, it is necessary to recalibrate even standard glassware, since the limits of precision within which standards institutions rightly confine their certificates are rather wide. The reference standard is then a single weight, or, better, a set of weights, calibrated after the method of HERBO[2], to which the capacities of the vessels are related in the process of checking. To keep the cumulative errors small, extremely good balances are needed. All the many corrections must be applied during this process, and the finer the limits the more detailed the corrections must be. A balance capable of dealing faithfully with the weights will not cope with the larger flasks and pipettes, and vessels over 100 ml furthermore call for weights beyond the normal range. Really accurate large balances and weights are not common items of equipment.

Temperature and drainage corrections can be eliminated by weight titrimetry, but large balances and weights are still needed, and moisture adsorption errors are a disadvantage.

Since analytical chemistry is solely concerned with ratios: the ratio of one thing to another, a part to the whole (percentage composition) one concentration to another (titrimetric factors), etc., and not with absolute masses, standard units are merely a routine convenience and not a necessity, and arbitrary reference standards can be used. Thus in the calibration of volumetric glassware, the reference standard is a piece of metal, or a number of pieces of metal, which commonly approximate to an integral weight, but could be any other durable object. This principle can conveniently be applied to eliminate many of the errors and disadvantages of titrimetry.

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* Paper read at the Symposium on Analytical Chemistry held by the Midlands Society for Analytical Chemistry at Birmingham in August 1954.

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ARBITRARY STANDARD WEIGHT TITRIMETRIC ANALYSIS

The numerous corrections can be almost entirely eliminated by a technique of arbitrary standard weight titrimetry. This can be practised if a large balance is available, but requires no large weights. It uses a sealed flask full of liquid as the reference standard instead of a metal weight. Since the solution is in the same type, size and shape of vessel as the reference standard, vacuum corrections are virtually eliminated also (*vide infra*), temperature corrections are not needed, and, as the surfaces are closely similar, adsorption errors are minimised. This method of elimination of adsorption errors is commonly applied in atomic weight work and in micro-analysis.

Vacuum weighing correction

When two solutions S_1 and S_2 are prepared by the method outlined below for inter titration, the flask plus solution in each case is poised against the reference standard, and therefore has in each case the same apparent weight in air as the standard.

Apparent weight of glass flask in air + apparent weight of S_1 in air
= Apparent weight of reference standard in air
= Apparent weight of glass flask + apparent weight of S_2 in air.

But the same flask is used in both cases, and its weight is constant.

$\therefore$ apparent weight of S_1 in air = apparent weight of S_2 in air.

If the true weights of the solutions are W_{s1} and W_{s2}, their densities are d_1 and d_2 and the density of air is d_a, then

$$W_{s1} - W_{s1} \times d_1 \times d_a = W_{s2} - W_{s2} \times d_2 \times d_a$$

$$\therefore \frac{W_{s1}}{W_{s2}} = \frac{1 - d_2 \times d_a}{1 - d_1 \times d_a}$$

The error incurred by ignoring vacuum correction will be

$$\frac{1 - \dfrac{W_{s1}}{W_{s2}}}{1} = \frac{d_a(d_2 - d_1)}{1 - d_1 d_a} \approx d_a(d_2 - d_1)$$

Solution densities can be calculated with sufficient accuracy from the approximate volume of solution prepared. For example, in preparing approximately 0.05*M* arsenic(III) and 0.01667*M* bromate the densities are 1.00362 and 1.00164 respectively, and, assigning a value of 0.00123 for the density of air, the error incurred is 2.44 in 10^6, or 0.00024%. Even with solutions very disparate in concentration and therefore density, the error is still very small, *e.g.* for aqueous dichromate, density 1.0025, and ferrous sulphate in 5*N* sulphuric acid, density 1.10, the error is still only 9 in 10^6, or 0.0009%.

When this correction is required, it can be calculated from the above equation.

METHOD

Flasks

Two vessels of suitable capacity are chosen as nearly alike as possible, preferably, though not necessarily, with long, narrow necks. Old volumetric flasks are convenient.

One should have a slightly longer neck and greater mass than the other to compensate for the glass removed in sealing. After cleaning, the heavier vessel is charged with a suitable amount of water and the neck smoothly sealed. This is the reference standard. For dealing with a wide range of non-aqueous solvents, the reference flask is charged with industrial spirit and chilled before sealing. A range of pairs of solution and reference flasks can readily be prepared, but they cannot readily be duplicated, so no units can be named.

Preparation of solutions

The material is weighed out normally, dissolved in a suitable solvent, suitably treated, cooled, the solution quantitatively transferred to the empty flask and diluted on a rough balance till 1–10 g lighter than the standard. The two flasks are similarly wiped off with a slightly damp cloth and then with a dry one, and placed in the balance case for about 30 min to allow adsorption equilibration; complete uniformity of temperature is not required, merely sufficient similarity to avoid affecting the balance by convection currents. The flasks are placed on the pans, and water or solvent added to the solution carefully, finally with a hair capillary, until the solution flask is a few milligrams the heavier. The beam is fully released, allowed to swing, and the oscillations observed. Solvent evaporates from the solution flask at a rate which can be regulated by quite crude humidity control in the balance case, and when the

TABLE I

MECHANICAL PRECISION OF SOLUTION PREPARATION ON A SPECIALLY CONSTRUCTED STANTON 2 kg PRECISION BALANCE

Solution prepared	*Weight of stoppered flask against counterpoise*	*Precision* %
2 l hydrazine sulphate, aqueous	16.3628	0.000 03
	16.3634	
2 l potassium bromate, aqueous	16.3630	
	16.3632	
1 l borax, aqueous	14.2866	0.000 02
	14.2866	
1 l potassium bromate, aqueous	14.2868	
	14.2867	
1 l ammonium bromide, ethanolic	15.6224	0.000 03
	15.6222	
1 l silver nitrate, methanolic	15.6223	
	15.6225	
½ l ammonium bromide, methanolic	6.5441	0.000 04
	6.5443	
½ l hydrochloric acid, aqueous	10.4888	0.000 04
	10.4890	
¼ l potassium dichromate, aqueous	3.5110	0.000 08
	3.5111	
¼ l potassium bromide, aqueous	3.5110	
	3.5112	

rest point reaches the zero point, the flask is removed, stoppered, and the contents mixed.

In this way balance to ± 1 mg is readily attained, and with careful working under controlled humidity, ± 0.1 mg has been attained on a specially constructed Stanton 2 kg precision balance with 2-l flasks. The maximum attainable precision is therefore 0.000 005%, while even on a 100-ml flask 0.001% is readily achievable. The precision has been checked by weighing the stoppered flask against its reference counterpoise; some figures are given in Table I. With cruder balances, weighing by substitution is effective.

Titrations

Titrations may be made directly to visual indicator (better photoelectric) end-points, or to preset electrometric end-points. Or the dilution technique may be used, which affords a finer control of reagent addition. To maintain maximum precision, approximately 1 g of solution weighed to ± 10 μg is diluted to 1 l in a calibrated flask, and the burette read to ± 0.01 ml (equivalent to titrating to 0.000 01 g). For this dilution it is advisable to take the weight titration to within 0.025 g of the end-point, which is quite simple, and gives a 25-ml titration, with 25 ml after the end-point.

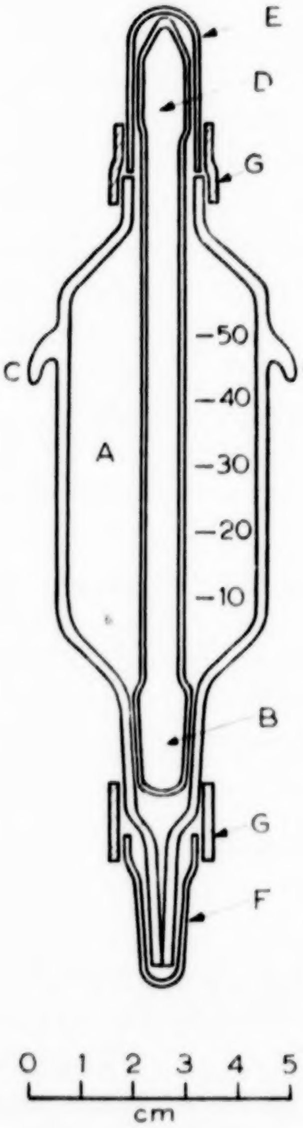

Fig. 1. Self-lubricating needle-valve weight burette. A. Burette bulb, capacity 60 ml; B. Ground in needle valve; C. Suspension hooks; D. Tubing of needle valve pinched flat at top to give finger grip; E. Glass cap: replaced by open tube for filling by suction: removed while manipulating valve; F. Glass jet cap; G. Thin rubber tubing.

Weight burettes

Most weight burettes are either clumsily heavy and have taps requiring lubrication[3,4], or are not susceptible to fine control[5,6]. The best answer appeared to be a tap lubricated by the solution, but totally enclosed to avoid loss. A needle-valve type of burette was developed as shown in Fig. 1. This calls for slightly different manipulation from an ordinary tap. A twist and push of the valve expels a quantity of solution, and very tiny drops can be ejected. It is filled by suction, or in the case of volatile solvents, under pressure. A pair are used, one the pipette, one the burette, in order to minimise adsorption errors. The two are charged and counterpoised, the pipette emptied, rehung and the loss in weight determined, the burette used, rehung and the change again determined. Vacuum weighing corrections are still required, though if the solutions are closely equivalent, the error incurred in neglecting this correction is very small, *e.g.*, in a 50-ml bromate–arsenic(III) titration it is 2 in 10^6.

TABLE II

MECHANICAL PRECISION OF OPERATIONS

Operation	*Errors*	*Precision of complete single operation*
a. At maximum attainable precision		
Weighing of sample	10 g weighed to 3 μg (0.000 03%)	0.000 06%
Preparation of solution	2 kg weighed to 0.1 mg (0.000 005%)	0.000 01%
Pipetting	50 g weighed to 10 μg (0.000 02%)	0.000 02%
Titration (i) direct	50 g weighed to 10 μg (0.000 02%)	0.000 02%
(ii) dilution	burette weighing, 50 g to 10 μg (0.000 02%) dilution of 1 g weighed to 10 μg (0.001 × 0.02%) to 1 l ± 0.03 ml (0.003 × 0.02%) and burette read to 0.01 ml (0.001 × 0.02%)	0.000 12%
Maximum theoretical precision per determination (i) direct		0.000 11%
(ii) dilution		0.000 21%
b. At lower precision		
Weighing of sample	10 g weighed to 0.01 mg (0.000 1%)	0.000 1%
Preparation of solution	100 g weighed to 1 mg (0.000 1%)	0.001 %
Pipetting	50 g weighed to 0.1 mg (0.000 2%)	0.000 2%
Titration (i) direct	50 g weighed to 0.1 mg (0.000 2%)	0.000 2%
(ii) dilution	Dilution as above, burette read to 0.1 ml	0.000 2%
	10 g diluted to 1 l, burette read to 0.01 ml	0.000 2%
	10 g diluted to 1 l, burette read to 0.01 ml	0.002 %

TABLE III

NEUTRALISATION REACTION

Titration of borax by hydrochloric acid, approximately 0.5*N*, prepared from constant boiling acid at 753 mm, reduced to vacuum. Results expressed as percentage of HCl, calculated assuming borax to be formula pure $Na_2B_4O_7 \cdot 10\ H_2O$.

	Direct titration to visual end-point	*Dilution titration photoelectric end-point*	*Direct titration to buffer pH (glass)*	*Dilution titration with glass electrode*
	20.2410	20.2382	20.2390	20.2374
	20.2362	20.2386	20.2372	20.2378
	20.2379	20.2378	20.2381	20.2377
	20.2344	20.2374	20.2368	20.2382
	20.2305	20.2379	20.2386	20.2378
Scatter	0.0105	0.0012	0.0028	0.0008
Precision	0.026%	0.005%	0.007%	0.002%
Mean	20.2360	20.2380	20.2379	20.2378

Uncertainty in the molecular weight of borax = 0.0055%.

The attainable precision

With moderate care, the operations of solution preparation can be accomplished to ± 0.000 1%, of pipetting and titration to 0.000 05%, and weighing of the materials for preparing solutions to 0.000 2% on 5–10 g samples. Table II shows first the maximum mechanical precision of measurement attainable by these methods, and secondly some examples of operations at lower, readily achievable orders of precision. For weighings below 100 g, a specially adjusted and modified Stanton CB3 balance with a sensitivity of 3 μg at 100 g was used.

Thus, *e.g.*, preparation of 100 ml of solution to a precision of 1 mg, and dilution titration with a 100-fold dilution of this, gives a precision of 0.003%.

The mechanical errors can therefore be reduced to the order of 1 or 2 parts per million. This proves to be considerably smaller than the errors due to chemical and physico-chemical phenomena, the purity of materials, and the discrimination of end-point, so permitting the investigation of these factors without hindrance.

TABLE IV[a]

PRECIPITATION REACTION

Titration of potassium bromide (from potassium bromate) by silver nitrate, approximately 0.1 *M*. Dilution titration, reference indicator electrode method[8], graphical potentiometric end-point.

Ratio Ag/O	*Atomic weight of silver*	*Ratio KBr/Ag*	*Molecular weight of KBr*
6.61744	107.8790	1.103217	119.0151
6.61758	107.8813	1.103170	119.0121
6.61751	107.8802	1.103201	119.0132
6.61738	107.8781	1.103162	119.0091
6.61731	107.8770	1.103191	119.0122
6.61770	107.8832	1.103179	119.0110
6.61760	107.8816	1.103229	119.0103
Scatter	0.0062		0.0060
Precision	0.003%		0.003%
Mean	107.8801		119.0119
International value	107.880		119.012

[a] Reproduced by kind permission of the Society for Analytical Chemistry, from the *Analyst*, 77 (1952) 679.

RESULTS

Under the most favourable circumstances, and working under atomic weight conditions as exemplified in the work of Hönigschmidt[7], the highest precision yet attained in a titrimetric process by the methods outlined is ± 0.001 5%. The accuracy is difficult to assess in this range, since the atomic weights concerned are not certainly known to greater accuracy, but may, in favourable circumstances, be said to reach 1 part per 100,000, or rougly one order less than the limiting mechanical precision of the measurements. Few determinations and methods of locating the end-point are capable of such precision, but certain selected and favourable reactions have been examined, and some results for each of three main types of titration are shown in Tables III to V.

TABLE V

REDOX REACTION

Titration of arsenious oxide by potassium bromate, approximately decinormal

	Direct titration to visual end-point	*Dilution titration photoelectric end-point*	*Direct titration to predetermined potential*	*Dilution titration graphical potentiometric*
Ratio of $KBrO_3$ to As_2O_3	1.00644	1.00637	1.00635	1.00638
	1.00661	1.00642	1.00627	1.00641
	1.00626	1.00638	1.00634	1.00639
	1.00655	1.00643	1.00645	1.00640
	1.00640	1.00640	1.00638	1.00641
Scatter	0.00035	0.00006	0.00018	0.00003
Precision	0.018%	0.003%	0.009%	0.0015%
Mean	1.00645	1.00640	1.00636	1.00640
Calculated ratio	1.00641. Uncertainty in molecular weights 0.0058%			

CONCLUSION

With the aid of suitable balances and weights, mechanical errors of measurement can be reduced to a level at least one order below the chemical error. Very few titrimetric reactions, indicators or electrometric methods of locating end-points justify a precision of measurement greater than that of ordinary titrimetric analysis, and, even in the most favourable cases, there is a limitation upon the chemical degree of precision attainable, which is set by physico-chemical factors such as adsorption and reaction equilibria, and it would appear that there is an ultimate degree of precision and accuracy, around that of present day atomic weights, beyond which it is not possible to progress by normal chemical methods.

ACKNOWLEDGEMENT

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SUMMARY

A technique of arbitrary standard weight titrimetric analysis has been proposed for realising the ultimate degree of mechanical precision of which titrimetric processes are capable, and has been applied to reactions and methods of end-point location which are particularly favourable. A form of needle-valve weight burette is also described.

It has been found that, even in the most favourable cases and working under the conditions of atomic weight determination, there is a limit to the precision and therefore accuracy of the analytical results, which is set by physico-chemical considerations, and which is at least one order less than the maximum attainable mechanical precision of measurement.

RÉSUMÉ

Une technique d'analyse titrimétrique employant un étalon arbitraire est proposée pour établir le degré de précision maximum des méthodes titrimétriques. On a trouvé que, même dans les cas les plus favorables, il existe pour les résultats analytiques une limite de précision déterminée par des considérations physico-chimiques et qui est inférieure à la précision mécanique des mesures.

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ZUSAMMENFASSUNG

Ein titrimetrisches Analyseverfahren mit einem willkürlichen Standardgewicht wurde zur Ermittlung der grösstmöglichen Genauigkeit titrimetrischer Methoden vorgeschlagen. Es hat sich herausgestellt, dass die Genauigkeit der analytischen Ergebnisse auf Grund physikalisch-chemischer Erwägungen begrenzt ist, und zwar liegt diese Grenze niedriger als die maximale mechanische Genauigkeit der Messungen.

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THE SEPARATION OF BERYLLIUM FROM POLYVALENT CATIONS WITH A DIALLYL PHOSPHATE COMPLEXING RESIN

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INTRODUCTION

In recent years a number of ion-exchange methods have been developed for separating beryllium from other polyvalent cations. In the earlier work[1,2] selective elution of the beryllium from other cations adsorbed on a sulphonated exchanger was conducted with solutions of inorganic acids or salts. However, it is evident that the relatively low resin affinity for beryllium, and its low selectivity (ratio of affinity for beryllium to affinity for other metals) renders such separations tedious if a number of different cations are present, and often requires a number of changes in eluting conditions before a separation is complete. More recently SCHUBERT *et al.*[3] have used sulphosalicylic acid (SSA) at pH 3.5–4.5 for the selective elution of beryllium from divalent cations, but as pointed out by these authors, trivalent cations such as aluminium are also eluted by SSA in this pH range. In a few instances, Na_2EDTA which complexes only weakly with beryllium[4], has been used[5] or its use suggested[3] as a masking agent for other polyvalent cations and this allows the beryllium to be selectively adsorbed by the resin. Even in this instance it can be expected that the gain in selectivity is likely to be offset considerably by the combined effects of competitive adsorption by the unsequestered sodium ions and the slight sequestering action of Na_2EDTA on the weakly adsorbed beryllium.

It has now been established that the complexing resin-sodium diallyl phosphate (NaDAP; $[(C_3H_5O)_2P(O)\ O\ Na^+]_n$)[6] adsorbs beryllium in the presence of Na_2EDTA to saturation capacity (*ca.* 4.9 mequiv./g of dry acid resin) irrespective of the aqueous phase beryllium concentration, while a large number of di- and trivalent cations are not adsorbed. The method thus allows the concentration of beryllium when the latter is only a minor or trace component in a mixture, and also the separation of the metal from minor contaminants.

EXPERIMENTAL

Resins

The NaDAP resin was prepared as previously described[6,7]. Its sodium–hydrogen exchange capacity was 4.93 mequiv./g dry H^+ form. The Zeo-Karb 225 (8–10% divinyl benzene) was obtained from Permutit Co. Ltd., London, and had a sodium–hydrogen exchange capacity of 4.68 mequiv./g of dry H^+ form. It was finally converted to the sodium form after a number of recycles between hydrochloric acid (0.5*N*) and sodium chloride (0.5*N*) solutions.

Analyses of beryllium

Beryllium when present in solution in relatively large concentrations and in the absence of fluoride ion, was estimated gravimetrically as the oxide after precipitation with ammonia. When fluoride was present the solutions were diluted (× 80 to 100 depending on the beryllium concentration) and assayed colorimetrically using *p*-nitrobenzene–azo–orcinol reagent[8]. Fluoride or Na_2EDTA do not interfere in these estimations, if present in low concentrations[9].

Adsorption and elution of beryllium

A column of NaDAP resin (8 cm deep × 1 cm diam.) which had a total sodium–hydrogen exchange capacity of 4.19 mequiv. was constructed. A solution of beryllium nitrate containing 0.68 mg/ml beryllium and whose pH had been adjusted to 4.0 with ammonia was then passed through at a flow rate of 0.45 ml/min. Analyses of fractions of the effluent indicated the point of breakthrough, and passage of solution was continued until no more beryllium was adsorbed. The column was then washed with water and elution of the beryllium was effected with ammonium fluoride (20 ml, 0.5*M*).

The total beryllium eluted was 4.11 mequiv. No beryllium was detected in solutions obtained on wet oxidizing the resin with a mixture of sulphuric and nitric acids. Separate experiments also indicated that nitric acid (20 ml, 1.0*N*) elutes the beryllium quantitatively from a similar bed of resin. Solutions of Na_2EDTA (2.5% w/v, 25 ml) or SSA (0.1*M*, 25 ml) at pH 4.0 failed to effect the elution of detectable beryllium ($\geqslant$1.0 mg) from the saturated resin. A similar experiment with a solution of beryllium (0.68 mg/ml) in the presence of Na_2EDTA (2.5% w/v) gave a breakthrough curve co-incident with that obtained in its absence. Also the beryllium capacity of the resin was the same (4.12 mequiv.), when the beryllium concentration of the solution phase was reduced to 0.1 mg/ml. Breakthrough curves were similarly obtained for a column of Zeo-karb 225 in the sodium form and of equal sodium capacity (4.19 mequiv.) to that of the column of NaDAP in the previous experiments. The saturation capacities of the resin bed for beryllium in the absence and presence of Na_2EDTA were 4.7 and 3.5 mequiv. respectively. Also elution with extra Na_2EDTA (2.5% w/v, 20 ml) which contained no beryllium effected a complete removal of the adsorbed beryllium from the resins.

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Separation of beryllium from other cations

A solution of Na_2EDTA (2.5%, 100 ml) at pH 4.0 and containing 2.5 mg of each of the following cations. Be^{+2}, Ca^{+2}, Sr^{+2}, Cu^{+2}, Zn^{+2}, Fe^{+3}, Al^{+3} and La^{+3}, was passed through a column of NaDAP (8 cm deep × 1 cm diam.) which had been previously washed with a solution of Na_2EDTA (2.5% w/v, 20 ml). After passage the column was again washed with Na_2EDTA solution (20 ml). Wet oxidation of the resin with sulphuric and nitric acids followed by analyses of the resulting solution showed that the beryllium was quantitatively adsorbed while no adsorption of the other cations took place. In separate experiments complete elution of the beryllium was effected with nitric acid (20 ml, 1.0*N*) or ammonium fluoride (20 ml, 0.5*M*). Analogous tests with solutions of Cd^{+2}, Hg^{+2}, Pb^{+2} and Mn^{+2} also showed that these cations are not adsorbed by NaDAP in the presence of Na_2EDTA.

DISCUSSION

Breakthrough of beryllium occurs almost immediately with Zeo-karb 225 (a monofunctional sulphonated resin) if the solution contains Na_2EDTA. Without the latter breakthrough occurs after the passage of *ca.* 6½ bed volumes of solution and the total capacity of the resin for beryllium was 4.7 mequiv. that is 0.5 mequiv. in excess of its sodium capacity. This increase in capacity may be due to some of the beryllium existing in the resin phase as $BeOH^+$. In the case of NaDAP (a monofunctional phosphorylated resin) the breakthrough curve and capacity for beryllium is not influenced by Na_2EDTA. Although distribution coefficients (K_d) for beryllium between the NaDAP resin and aqueous phases containing Na_2EDTA have not been measured, the absence of detectable beryllium from Na_2EDTA solutions which have been passed through a beryllium saturated column suggests very high K_d values. In conformity with the law of mass action K_d should increase further to a constant maximum as the beryllium loading on the resin decreases. Also SSA which forms a stable complex with beryllium [$\log K^{M}_{MHL} \sim 4.9$][10] and which readily elutes it from Dowex-50 (a sulphonated resin)[3], fails to elute it from NaDAP. On the other hand Na_2EDTA effects complete elution of the beryllium from Zeo-karb 225.

As the saturation capacity of NaDAP for beryllium is equal to that for sodium the adsorption mechanism is

$$Be^{+2} + 2NaDAP \rightleftharpoons Be(DAP)_2 + 2Na^+$$

The very high affinity of the NaDAP compared to sulphonated resins for beryllium also suggests that the latter is bound as a complex to the phosphate functional unit, but speculation on structure of complex would be premature at this stage.

As well as the polyvalent cations listed here from which beryllium was separated, it is also evident that it can be separated from bismuth and polonium(IV) under the same conditions[11,12]. Magnesium is not readily eluted with Na_2EDTA from NaDAP, but it can be completely eluted with the disodium salt of cyclohexane-1,2-diaminetetraacetic acid which is a stronger sequestering agent[13]. As with Na_2EDTA, beryllium is not eluted with this reagent from NaDAP. Uranium(VI) (UO_2^{+2}) like beryllium is also quantitatively adsorbed by the resin in the presence of Na_2EDTA. Sodium carbonate however effects its quantitative elution, while the beryllium is retained on the resin bed, probably as an insoluble basic carbonate.

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SUMMARY

The complexing polymer sodium diallyl phosphate (NaDAP) when used in conjunction with disodium ethylene diamine tetraacetate (Na_2EDTA) separates beryllium quantitatively from alkaline earths (Ca and Sr), ferric and divalent cations of the first transitional period, aluminium and lanthanides, cadmium and mercury(II), bismuth and polonium(IV). The high affinity of NaDAP for beryllium should permit its concentration by several orders of magnitude, when present as a minor or trace component in a mixture of polyvalent cations. The results are compared with those obtained using sulphonated resin.

RÉSUMÉ

L'allylphosphate de sodium polymère, en présence d'éthylènediaminetétracétate disodique, permet de séparer quantitativement le glucinium d'avec de nombreux autres cations. Les résultats sont comparés avec ceux obtenus à l'aide d'une résine sulfonée.

ZUSAMMENFASSUNG

Polymeres Diallyl-natriumphosphat, in Gegenwart des Dinatriumsalzes der Äthylendiamintetraessigsäure ermöglicht eine quantitative Abtrennung des Berylliums von zahlreichen mehrwertigen Kationen. Die Ergebnisse werden mit denjenigen, die mit Hilfe eines sulfonierten Harzes erhalten wurden, verglichen.

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SOLUBILITY PRODUCT RELATIONS IN THE RARE EARTH HYDROUS HYDROXIDES

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This paper is being presented to consider the solubility products of the rare earth hydroxides. A considerable amount of work has been directed to this topic[1]. The difference between "new" and "old" precipitated hydroxides has already been well established and seems to be a kinetic phenomenon in which a more soluble material undergoes ripening through dehydration and further crystalization to become more insoluble. However, there has been some question regarding the solubility product as effected by temperature. This paper deals with this point for the freshly precipitated hydroxides. An approximation is also offered to the thermodynamic heat of solution of these precipitates.

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The study was carried out by dissolving a preweighed sample of ignited oxide in a slight excess of standard perchloric acid*. This solution was then titrated with increments of standard sodium hydroxide. Readings were taken after each increment of sodium hydroxide when the pH had come to equilibrium while the temperature was held within 0.2°. This was generally accomplished in about 2 min. In this manner a curve of the type shown in Fig. 1 was obtained by recording the pH as a function of the base added. In Fig. 1, point A represents the end-point of excess perchloric acid; B, the end-point corresponding to complete precipitation of the rare earth hydroxide; and C represents the point (B—A)/2. For varying temperature a family of curves was obtained, as shown in Fig. 2, with $T_1 > T_2 > T_3$. By use of the pH at C, the hydroxyl concentration was obtained. By use of the fact that the concentration of rare earth in solution at point C is one-half that at A, the solubility product was obtained by substitution in:

$$L_{\text{R.E.(OH)}_3} = (\text{R.E.})\,(\text{OH})^3$$

By use of the Van 't Hoff isochore and the assumption that $L_{\text{R.E.(OH)}_3}$ represents the equilibrium between solid and solution:

$$\text{Solid}_{\text{R.E.(OH)}_3} \rightleftarrows \text{ionized solution}_{\text{R.E.(OH)}_3}$$

the heat of the solution was calculated.

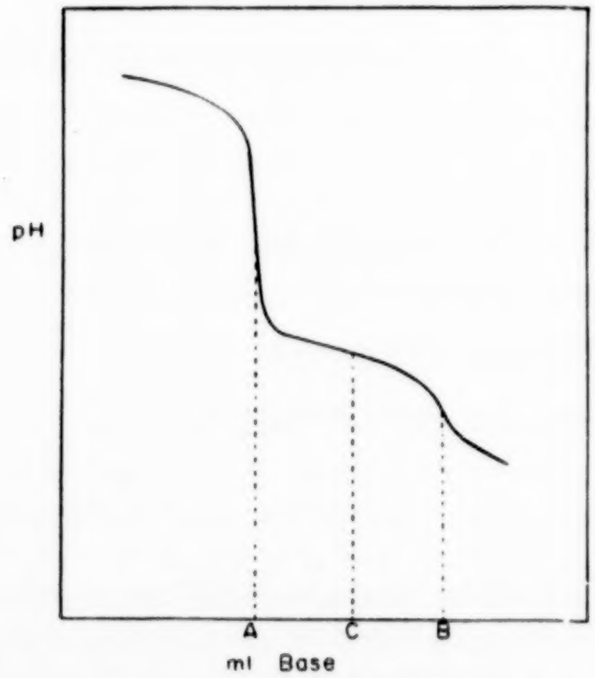

Fig. 1. Typical titration curve.

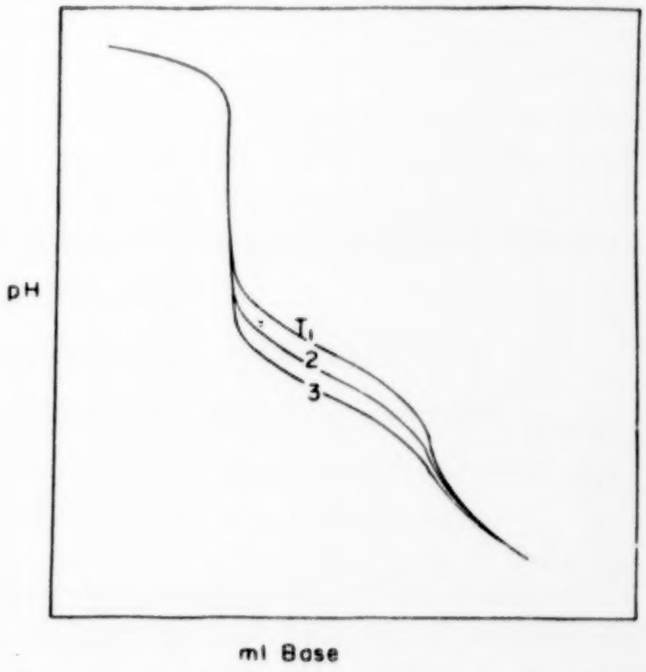

Fig. 2. Typical titration curve for variation in temperature.

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* Rational atomic weights are determined by this means as:

$$\text{At. Wt. R} = \frac{\dfrac{\text{Wt. R}_2\text{O}_3 \times 6000}{\text{mequiv. H}^+ \text{ equal to R}_2\text{O}_3} - 48}{2}$$

The data was obtained with a Beckman model H-2 pH meter. A Cenco Universal Relay Control and mercury contact thermostat regulated the temperature in a 10-gallon water bath. By this means the pH could be obtained to within 0.02 pH units and the temperature to within 0.2°. The rare earths had the following purities (with major impurities) as indicated by the manufacturers: La 99.9% (Ce, Pr), Pr 99.9% (Ce, Nd), Nd 99.0% (Pr, Sm), Sm 99.0% (Gd, Eu), Gd 98% (Sm, Nd, Dy), Y 99.0% (Dy, Gd).

TABLE I

SOLUBILITY PRODUCT DATA OF RARE EARTH HYDROXIDES

Rare earth	*T°C*	*Rare earth at point C*	*pH at point C*	*Solubility product*
La	10	$5.48 \cdot 10^{-3}$	9.10	$14 \cdot 10^{-18}$
	20	$5.48 \cdot 10^{-3}$	8.68	$0.64 \cdot 10^{-18}$
	30	$5.48 \cdot 10^{-3}$	8.55	$0.25 \cdot 10^{-18}$
	40	$5.48 \cdot 10^{-3}$	8.10	$11 \cdot 10^{-21}$
Pr	10	$2.82 \cdot 10^{-2}$	8.23	$14 \cdot 10^{-20}$
	20	$2.82 \cdot 10^{-2}$	8.02	$3.3 \cdot 10^{-20}$
	30	$2.82 \cdot 10^{-2}$	7.77	$5.8 \cdot 10^{-21}$
	40	$2.82 \cdot 10^{-2}$	7.62	$2.4 \cdot 10^{-21}$
Nd	10	$3.72 \cdot 10^{-2}$	8.17	$12 \cdot 10^{-20}$
	20	$3.72 \cdot 10^{-2}$	7.90	$1.9 \cdot 10^{-20}$
	30	$3.72 \cdot 10^{-2}$	7.77	$7.61 \cdot 10^{-21}$
	40	$3.72 \cdot 10^{-2}$	7.65	$3.24 \cdot 10^{-21}$
Sm	10	$4.47 \cdot 10^{-2}$	7.82	$1.3 \cdot 10^{-20}$
	20	$4.47 \cdot 10^{-2}$	7.54	$2.0 \cdot 10^{-21}$
	30	$4.47 \cdot 10^{-2}$	7.32	$39 \cdot 10^{-23}$
	40	$4.47 \cdot 10^{-2}$	7.07	$7.2 \cdot 10^{-23}$
Gd	10	$1.21 \cdot 10^{-2}$	8.08	$2.3 \cdot 10^{-20}$
	20	$1.21 \cdot 10^{-2}$	7.86	$0.46 \cdot 10^{-20}$
	30	$1.21 \cdot 10^{-2}$	7.48	$35 \cdot 10^{-23}$
	40	$1.21 \cdot 10^{-2}$	7.25	$6.8 \cdot 10^{-23}$
Y	10	$3.75 \cdot 10^{-2}$	7.74	$6.2 \cdot 10^{-21}$
	20	$3.75 \cdot 10^{-2}$	7.65	$3.3 \cdot 10^{-21}$
	30	$3.75 \cdot 10^{-2}$	7.31	$32 \cdot 10^{-23}$
	40	$3.75 \cdot 10^{-2}$	7.10	$7.3 \cdot 10^{-23}$

TABLE II

RELATIVE BASICITY OF RARE EARTH HYDROXIDES

Ratio	*10°C*	*20°C*	*30°C*	*40°C*
La : Y	2270	192	770	150
Pr : Y	22.8	9.95	18.2	33.2
Nd : Y	19.7	5.57	23.8	44.3
Sm : Y	2.12	0.59	1.23	0.98
Gd : Y	3.67	1.38	1.09	0.92
Y : Y	1.00	1.00	1.00	1.00

TABLE III

HEATS OF SOLUTION OF RARE EARTH HYDROXIDES

Rare earth	*Temperature interval*	*ΔH°(kcal)*
La	10–20	1.27
	20–30	0.42
	30–40	1.46
Pr	10–20	0.59
	20–30	0.75
	30–40	0.41
Sm	10–20	0.77
	20–30	0.72
	30–40	0.80
Gd	10–20	0.65
	20–30	1.13
	30–40	0.55
Nd	10–20	0.77
	20–30	0.44
	30–40	0.40
Y	10–20	0.25
	20–30	1.03
	30–40	0.69

Table I gives the major result of this work, giving vital data and calculated solubility product of the rare earth hydroxides. To be noted is the greater solubility for the greater atomic radii and lower temperature. It is fully recognized that these values do not represent equilibrium solubility data, but rather are to be associated only with the "new" hydroxide before it has had the opportunity to ripen. Table II shows the relative basicities as compared to yttrium hydroxide (comparison between like temperatures). This quite aptly characterizes the basicity which increases with increasing atomic radii and lower temperature. Table III shows the heat of solution for each hydroxide studied. It is estimated to be accurate to about 20%, considering temperature stability and accuracy in pH.

SUMMARY

The solubility products for some rare earth hydroxides and their temperature dependence have been shown. Greater solubility is shown for larger atomic radii and for lower temperature.

RÉSUMÉ

Les produits de solubilité de quelques hydroxydes de terres rares ont été déterminés.

ZUSAMMENFASSUNG

Es wird über die Löslichkeitsprodukte der Hydroxyde einer Anzahl seltener Erden berichtet.

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CHELOMETRIC TITRATION OF CALCIUM USING A MIXED INDICATOR*

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INTRODUCTION

A problem often encountered in working with small amounts of clays is the determination of microgram quantities of calcium. The indicators now used for macrodeterminations are not suitable for determining very small quantities of calcium.

Recently Eriochrome Blue S.E.[1], Disodium salt of 3-(5-chloro-2-hydroxy-phenylazo)-4,5-dihydroxynaphthalene-2,7-disulfonic acid, used with a green screening dye (Naphthol Green B), was proposed as an indicator for the microtitration of calcium in deproteinized blood. The addition of the green dye greatly aids in the detection of the end-point.

This investigation reveals that this "mixed" indicator is suitable for the chelometric titration of calcium in clays and soils. Only manganese and strontium interfere with the end-point in the presence of potassium cyanide. Methyl alcohol aids in the detection of the end-point in semimicro titrations, but no improvement was observed for macrotitrations.

EXPERIMENTAL

In preliminary investigations certain metals interfered with the titration and/or end-point. Therefore it was necessary to study the effect of methyl alcohol and potassium cyanide on the titration of calcium using the proposed indicator. Thus a known amount of calcium, methyl alcohol, and potassium cyanide were placed into 150-ml pyrex beakers singly and in combination to determine both the individual and combined effect of methyl alcohol and potassium cyanide. After placing these components into beakers, 2 ml of 10% potassium hydroxide was added to raise the pH above 12. Next the indicator, 6 drops of 0.1% Naphthol Green B in 25% methyl alcohol, and 6 drops of 0.1% Eriochrome Blue S.E. in 25% methyl alcohol, was added. The volume was adjusted to 30 ml and titrated with EDTA (disodium salt of ethylenediaminetetraacetic acid) until the color of the solution changed from a "dirty" red to blue.

Results from this first study led to the following semimicro chelometric titration: Place the solution containing the calcium into a pyrex beaker, add 15 ml of absolute methyl alcohol, 2 ml of 10% potassium hydroxide, 200 mg of potassium cyanide, and then add 6 drops each of 0.1% Naphthol Green B and Eriochrome Blue S.E. Titrate the solution with EDTA.

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* Arizona Agricultural Experiment Station Technical Paper No. 491.

** A portion of a thesis to be submitted by the senior author in partial fulfillment of the requirements for the Ph. D. degree.

The above procedure was used to study the effect of several ions on the end-point. The other ions were added prior to the addition of the methyl alcohol.

This method also was used to determine calcium in solutions in equilibrium with various calcium-clay samples. Centrifugation was used to remove the clay from the suspension and an aliquot of the solution was treated as described in the proposed method.

A final study was conducted to determine how the indicator, Calver II, used in the EDTA titration of macro-amounts of calcium[2], compared to this mixed indicator for the titration of exchangeable calcium from a soil sample. The test solution was prepared by leaching 10 g of soil with 200 ml of neutral normal ammonium acetate, evaporating to dryness, digesting the residue with nitric and perchloric acids[3], and making the solution to volume. The phosphorus was removed from a portion of this solution by passing it through an anion-exchange column (15 by 70 mm) and eluting with 30 ml deionized water. The column was filled with the nitrate form of Dowex-1 X8 (50 to 100 mesh). The sample plus the water washings were made to volume and an aliquot was used for the determination of calcium with each of the two indicators. The procedure followed was the same as with the semimicro titrations except that methyl alcohol was not used.

TABLE I

SEMIMICRO CHELOMETRIC TITRATION OF CALCIUM IN THE PRESENCE OF POTASSIUM CYANIDE AND METHYL ALCOHOL USING A MIXED INDICATOR

Treatment of solution	*Calcium present (μg)*	*Calcium found[a] (μg)*
None	10.0	10.0
200 mg KCN	10.0	10.1
15 ml methanol	10.0	10.3
200 mg KCN and 15 ml methanol	10.0	10.0

[a] Mean of 3 titrations.

RESULTS AND DISCUSSION

As shown in Table I, addition of potassium cyanide and methyl alcohol did not interfere with the titration of calcium using the proposed mixed indicator. In the presence of copper the apparent end-point is obtained without the addition of any EDTA unless the potassium cyanide is present. Thus it is necessary to add potassium cyanide prior to the addition of the indicator. Methyl alcohol made the change in color much more visible in the semimicro titrations, therefore it is recommended in the semimicro titrations of calcium using the mixed indicator.

The only ions studied which affected the end-point in the proposed method were manganese and strontium, Table II. Manganese decreased the amount of calcium found but strontium appeared to titrate as calcium. It is doubtful that in plants and soils amounts of manganese large enough to interfere will be found with very small amounts of calcium.

Three samples, of solutions in equilibrium with a clay, were titrated to determine the calcium present, and the precision of the method for this type of titration. The method was satisfactory as shown in Table III, with a good visible end-point.

The proposed mixed indicator compared satisfactorily with Calver II in calcium

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TABLE II

SEMIMICRO CHELOMETRIC TITRATION OF CALCIUM IN THE PRESENCE OF VARIOUS IONS USING A MIXED INDICATOR

Calcium present (μg)	*Other ion present (μg)*	*Calcium found[a] (μg)*
10.0	50.0 Magnesium	10.4
20.0	50.0	20.3
30.0	50.0	30.6
10.0	50.0 Copper	10.1
20.0	50.0	20.0
30.0	50.0	30.5
10.0	50.0 Zinc	10.3
20.0	50.0	19.4
30.0	50.0	29.6
10.0	50.0 Phosphorus	10.1
20.0	50.0	19.3
30.0	50.0	29.3
10.0	50.0 Iron	10.3
20.0	50.0	19.3
30.0	50.0	29.7
10.0	50.0 Cobalt	10.2
20.0	50.0	19.6
30.0	50.0	30.0
10.0	50.0 Aluminum	10.2
20.0	50.0	19.8
30.0	50.0	29.5
10.0	50.0 Manganese	9.4
20.0	50.0	17.7
30.0	50.0	25.6
10.0	30.0 Strontium	23.3
20.0	30.0	33.1
30.0	30.0	42.4

[a] Mean of 3 titrations.

TABLE III

SEMIMICRO CHELOMETRIC TITRATION OF CALCIUM IN EQUILIBRIUM SOLUTION OF CLAY SAMPLES USING A MIXED INDICATOR

Sample number	*Calcium found (μg)*
1.	25.6
	25.1
	24.9
	25.3
Mean	25.2
2.	29.8
	29.5
	30.1
	29.7
Mean	29.8
3.	20.1
	20.3
	19.8
	20.3
Mean	20.1

recovered, Table IV, in the visibility of the end-point, and was superior in the stability of the indicator. Calver II fades rapidly after the completion of the titration but the mixed indicator maintained its color for 4 hours or longer.

Preliminary investigations reveal that the proposed indicator may be used in the chelometric titration of magnesium after calcium has been removed.

TABLE IV

COMPARISON OF MIXED INDICATOR WITH CALVER II FOR CHELOMETRIC TITRATION OF EXCHANGEABLE SOIL CALCIUM

Sample number	*Calcium found[a] (mg) Calver II*	*Calcium found[a] (mg) Mixed indicator*
1.	0.56	0.59
2.	0.56	0.59
3.	0.56	0.58
4.	0.61	0.59
5.	0.59	0.58
6.	0.60	0.58
7.	0.59	0.59
8.	0.60	0.61
9.	0.60	0.58
10.	0.59	0.59
11.	0.58	0.57
12.	0.57	0.57

[a] Mean of 2 titrations

ACKNOWLEDGEMENTS

This study was supported in part by a grant from California Spray Chemical Corporation, Richmond, Calif. Experimental samples of Eriochrome Blue S.E. were supplied by Geigy Chemical Corporation, Ardsley, N.Y., and the Dowex-1 X8 was supplied by Dow Chemical Company, Midland, Mich. The cooperation of the above companies is gratefully acknowledged.

SUMMARY

A mixed indicator for the chelometric titration of calcium has promise for the determination of microgram amounts of calcium in the presence of relatively high concentrations of other ions. Potassium cyanide eliminates the interference of certain metals. Addition of methyl alcohol improves the visibility of the end-point in a semimicro titration of calcium, although it does not improve the end-point for macro titrations.

This indicator also may be useful in the determination of magnesium after calcium has been removed from the sample.

RÉSUMÉ

Un indicateur mixte est proposé pour le microdosage complexométrique du calcium, en présence de nombreux autres ions. Il peut être utilisé également pour le dosage du magnésium, en l'absence de calcium.

ZUSAMMENFASSUNG

Zur Komplexometrischen Mikrobestimmung von Calcium in Gegenwart grösserer Mengen anderer Ionen wird ein Mischindikator vorgeschlagen, der auch zur Bestimmung von Magnesium in Abwesenheit von Calcium verwendet werden kann.

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ULTRAVIOLET ABSORPTION SPECTRA OF *α*-NITROSO-*β*-NAPHTHOL AND ITS COPPER CHELATE

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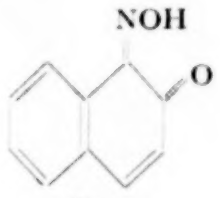
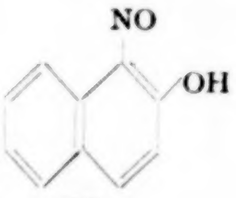
Although *α*-nitroso-*β*-naphthol was the first organic compound to be used for the analytical determination of a number of metal ions (especially Co) the structures of these metal complexes are not quite clear. The difficulty in assigning correct structures to these compounds lies in the fact that *α*-nitroso-*β*-naphthol itself may have two alternative structures (I) and (II) and no direct evidence is yet available to ascertain which one might represent the active form of this substance.



(I)



(II)

In the present work an attempt has been made to obtain some information in this respect from the measurement of the U.V. absorption spectra of *α*-nitroso-*β*-naphthol and its copper chelate. The same method was previously used by the author[1–3] for the determination of the nature of the bond between the metal atom and the organic ligand in the case of the chelates of acetyl acetone and quinoline-8-carboxylic acid.

Of the two possible structures of *α*-nitroso-*β*-naphthol (I) is quinonoid while (II) is benzenoid and these two forms should have completely different absorption spectra. The benzenoid form will have an absorption spectrum similar to naphthalene, in addition to some new bands due to localized transitions on the substituent and to charge migration between the π electrons on the ring and the substituent group. On the other hand the absorption spectrum of the quinonoid form will be rather broad and diffuse with no structure at all. The absorption band will be located below 300 mμ in the region where the absorption due to *α*-,*β*-unsaturated ketones appears. In addition there will invariably be an absorption band located at the longer wavelength side which may be associated with $n \rightarrow \pi^*$ transition having an intensity much less than the short-wave band.

It is evident from Fig. 1 that the absorption spectra of *α*-nitroso-*β*-naphthol in ethanol is more like that of a quinonoid compound than a benzenoid one, suggesting that structure (I) predominates in the benzenoid–quinonoid resonance of the system in ethanol. FEIGL[4] suggested that (I) is converted into (II) in acidic medium. In 0.1*N* ethanolic perchloric acid the spectrum of *α*-nitroso-*β*-naphthol is not affected at all (Fig. 2). In 0.1*N* ethanolic KOH, however, the spectrum is profoundly changed

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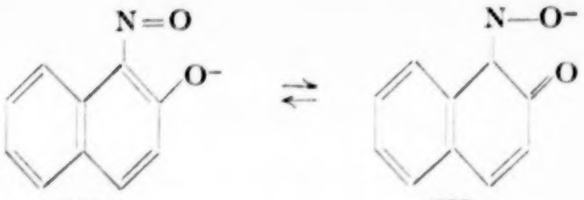
(Fig. 2). The absorption spectrum in this medium closely resembles that of *β*-naphthol in alkaline medium (Fig. 3). In addition there is a weak absorption band at 425 m*μ* which may be associated with charge resonance between (III) and (IV).



(III) (IV)

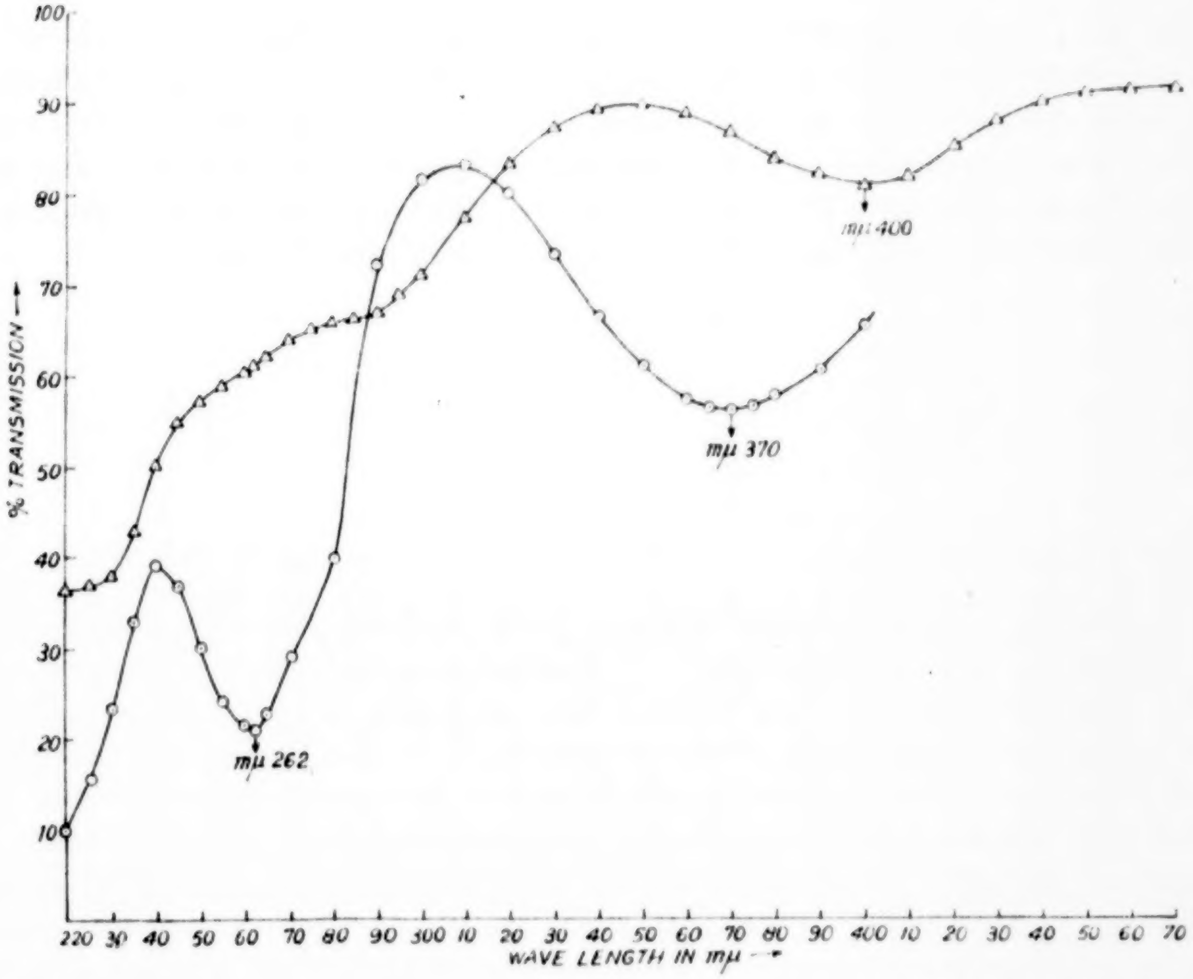
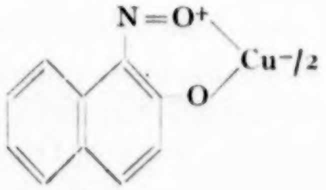


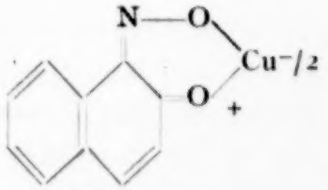
Fig. 1. U.V. absorption curves of *α*-nitroso-*β*-naphthol (○) and its Cu chelate (△), in ethanol.

That the change in alkaline medium is not due to any permanent alteration in the structure of *α*-nitroso-*β*-naphthol is shown by the fact that when the alkali is neutralised the spectrum reverts to the original form in neutral ethanol.

The structure of the copper chelate is represented as



or



(V) (VI)

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In structure (VI), as the lone pair electrons of the oxygen undergo partial fixation, we expect the $n - \pi^*$ band, *i.e.* the long-wave band of α-nitroso-β-naphthol, to shift towards the blue. In practice we notice (Fig. 1) a shift in the 370-mμ band towards the red to 400 mμ. The structure of the long-wave band is rather similar to the long-wave band of α-nitroso-β-naphthol in ethanolic KOH. This indicates that in the copper chelate the structures (V) and (VI) are present in almost equal amounts. The planarity of the molecule in the copper chelate will undoubtedly facilitate the charge resonance envisaged in (V) and (VI).

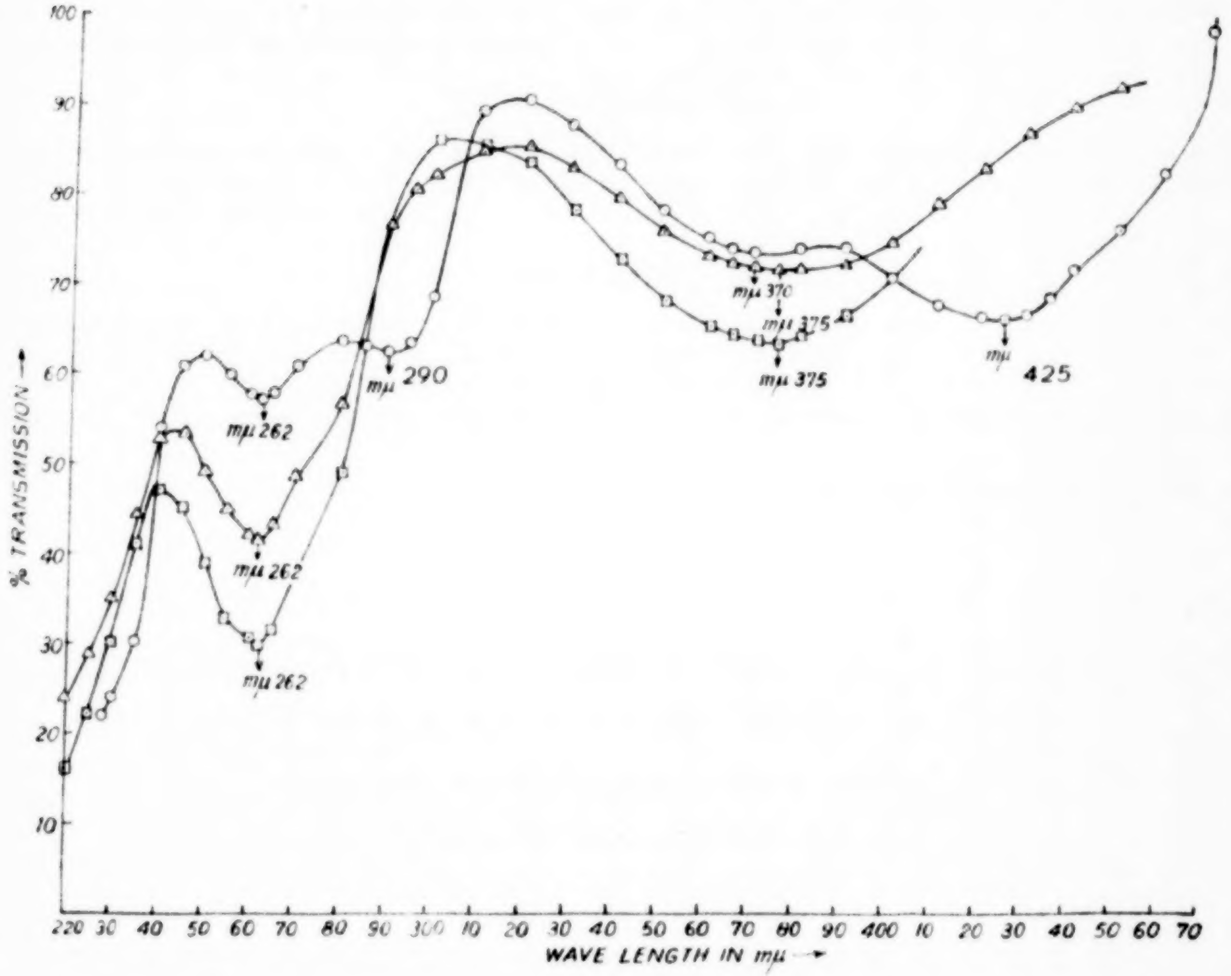

Fig. 2. U.V. absorption curves of α-nitroso-β-naphthol, (□) in 0.1N ethanolic $HClO_4$, (○) in 0.1N ethanolic KOH, (△) after neutralisation of the alkaline solution with 0.1N ethanolic $HClO_4$.

Ultraviolet absorption measurements were carried out with the help of the Beckman model D.U. quartz spectrophotometer using a 1-cm quartz absorption cell. The ethanol used was refluxed for 6–8 h with solid caustic soda and then distilled. It showed complete transmission down to 220 mμ. Purification of α-nitroso-β-naphthol was carried out in the following way. 1 g of Schering-Kahlbaum's A.R. α-nitroso-β-naphthol was dissolved in 100 ml of spectroscopically pure ethanol and the solution was passed several times through fresh columns of E. Merck's Brockman alumina (8 cm × 0.5 cm). Each treatment was followed by spectrophotometric examination of the substance in solution till no variation in its U.V. absorption curve was noted.

A portion of the ethanolic solution was immediately employed for absorption measurement of the ligand in neutral, acidic, and alkaline media, while the other part was used in the preparation of the copper complex. (In the copper complex the percentage of the metal was found to be somewhat higher than the theoretical value. Such a

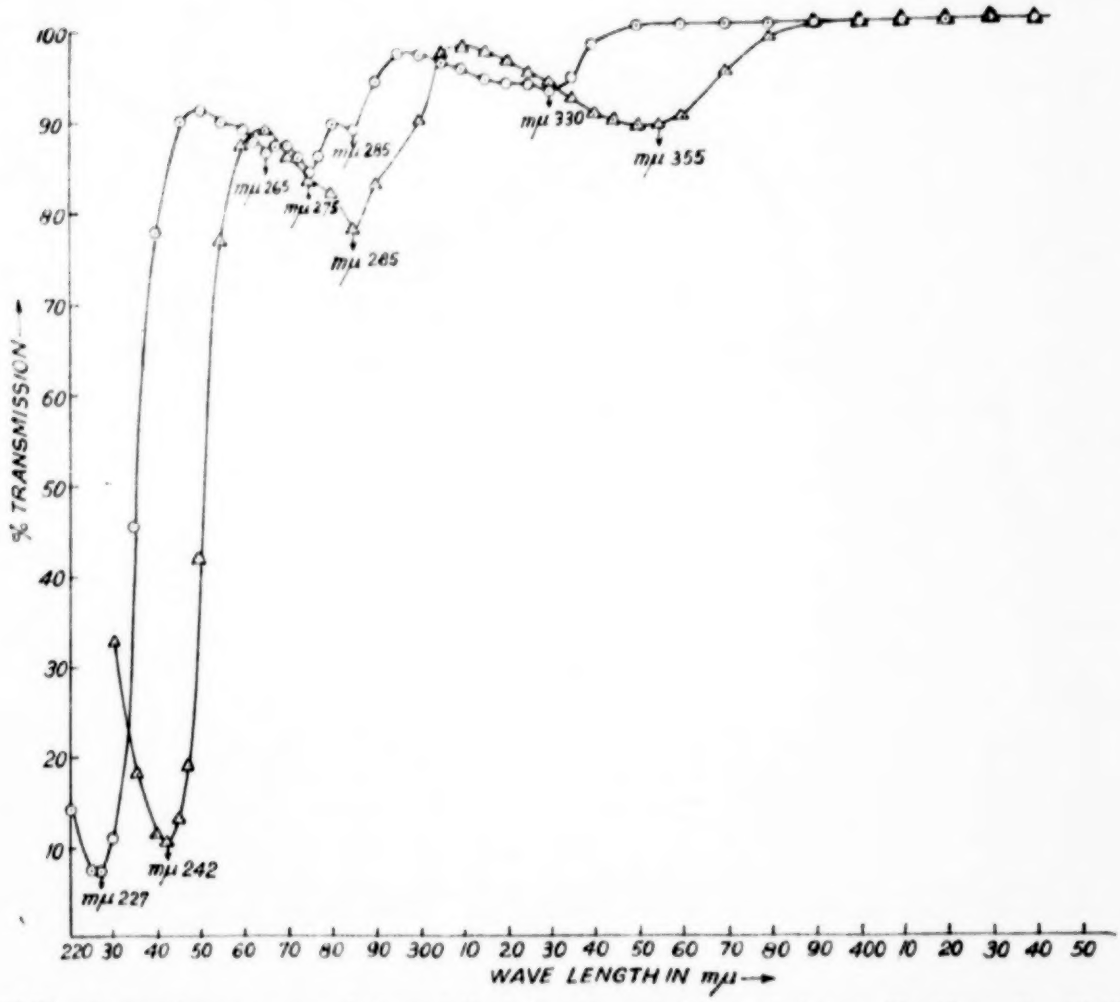

Fig. 3. U.V. absorption curves of β-naphthol in ethanol (○), and in 0.1N ethanolic KOH (△).

discrepancy is, however, well known for the chelates of α-nitroso-β-naphthol, a reason why they have often been regarded as salt-type associated compounds. This assumption is ruled out by the fact that the absorption curve of the chelate shows no indication of unaffected ligand molecule, and as such the cause of the discrepancy in the analytical results should be looked for elsewhere.) E. Merck's β-naphthol was purified by recrystallising twice from spectroscopically pure ethanol. Solutions employed for absorption measurements were 10^{-4}–$10^{-5}M$.

ACKNOWLEDGEMENT

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SUMMARY

From a comparative study of the U.V. absorption spectra of α-nitroso-β-naphthol and of β-naphthol in neutral ethanol and in the presence of 0.1*N* $HClO_4$ and 0.1*N* KOH respectively, evidence in favour of the quinone-oxime structure of α-nitroso-β-naphthol has been presented. The spectrum of the copper chelate of α-nitroso-β-naphthol indicates a planar configuration of the complex with considerable resonance between the quinonoid and benzenoid structures of the ligand.

RÉSUMÉ

On a effectué une étude des spectres d'absorption dans l'ultra-violet du β-naphtol, de l'α-nitroso-β-naphtol, et de son chélate avec le cuivre, en vue d'en établir la structure.

ZUSAMMENFASSUNG

Es wird versucht, aus den U.V.-Absorptionsspektren von β-Naphthol und α-Nitroso-β-naphthol in saurem und alkalischem Medium sowie des Kupferkomplexes von α-Nitroso-β-naphthol Rückschlüsse auf deren Struktur zu ziehen.

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THE DETERMINATION OF COBALT, IRON PLUS VANADIUM OR MANGANESE IN SOFT MAGNETIC ALLOYS

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Soft magnetic alloys have been developed which consist nominally of 48% of iron and cobalt and the balance of manganese or vanadium. These materials are useful because of their high saturation values. Vanadium and manganese have been added to facilitate the cold-working of the material.

The chemical analysis of these materials for iron, and manganese or vanadium is relatively simple. Iron may be determined conveniently by the conventional reduction with stannous chloride followed by titration with potassium dichromate using diphenylamine sulfonate as an indicator. Manganese may be determined by oxidation with peroxydisulfate in the presence of silver ion followed by the addition of a measured excess of ferrous sulfate and a back titration with potassium permanganate. Vanadium may be determined by the ferrous sulfate–peroxydisulfate method.

The determination of cobalt, however, presents some difficulty. Gravimetric methods are unattractive because of the high percentage of cobalt. The volumetric methods available for cobalt require a preliminary separation for these alloys.

In view of the successful application of ion exchange separations in conjunction with EDTA titrations in metallurgical analysis, a similar approach was taken for the determination of cobalt in these alloys.

The separation of iron and cobalt using a strongly basic anion exchange resin in hydrochloric acid medium has already been accomplished. **KRAUSE AND MOORE** have shown that manganese(II) and vanadium(IV) are not absorbed on a resin of this type in $9N$ hydrochloric acid[1,2]. Iron(III) and cobalt are both strongly absorbed under these conditions[3].

Solutions of cobalt, iron, manganese and vanadium were prepared so as to be able to approximate the content of an alloy by taking appropriate aliquots.

The solutions were standardized by adding somewhat more than the equivalent amount of EDTA and back titrating with a standard copper solution using calcein as fluorescent indicator[4]. The titrations were carried out under ultraviolet light using an apparatus previously described[4].

The column separation was performed by mixing appropriate aliquots of the standard solutions. The mixtures were evaporated nearly to dryness and diluted to approximately 10 ml with $9N$ hydrochloric acid. The solutions were transferred to an anion exchange column with $9N$ hydrochloric acid. Vanadium or manganese was eluted with $9N$ hydrochloric acid, cobalt with $4N$ hydrochloric acid, and iron with $0.5N$ hydrochloric acid. The values shown in Table I were obtained using the procedure given below for alloys.

TABLE I

Co present[a]	*Co found*	*Fe present*[a]	*Fe found*	*V present*[a]	*V found*	*Mn present*[a]	*Mn found*
51.8	51.8	32.2	32.1	—		16.0	16.0
51.8	51.7	32.2	32.1	—		16.0	16.0
51.8	51.8	32.2	32.4	—		16.0	15.9
51.8	51.8	32.2	32.2	—		16.0	16.1
51.8	51.7	32.2	32.2	—		16.0	16.1
49.3	49.3	44.2	44.1	6.49	6.50	—	
49.3	49.2	44.2	44.2	6.49	6.53	—	
49.3	49.3	44.2	44.2	6.49	6.52	—	

[a] Nominal values for iron, vanadium and manganese by classical methods. Cobalt value by difference.

PROCEDURE

Dissolve a 1-g sample in 10 ml of hydrochloric acid, $9N$. After the sample is dissolved add 5 drops of 30 vol.% hydrogen peroxide and boil for 10 min. Add 0.1 g of sodium sulfite and boil for 10 min. Transfer the solution to a 100-ml volumetric flask and dilute to volume with $9N$ hydrochloric acid. Transfer a 10-ml aliquot to an anion-exchange resin containing Dowex-1, (100–150 mesh, chloride form) previously washed with $9N$ hydrochloric acid. After rinsing the sample on to the resin elute the manganese or vanadium with 30 ml of $9N$ hydrochloric acid into a 250-ml beaker. Place a clean beaker under the column and elute with $4N$ hydrochloric acid until the blue cobalt band is removed from the column. After the cobalt has been removed from the column elute with $0.5N$ hydrochloric acid until the yellow iron band is removed.

Evaporate each fraction to a few ml, add 50 ml of water, and 10 ml of sodium

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acetate–acetic acid buffer (for manganese, use ammonium acetate buffer). Add an excess of EDTA, adjust the pH to approximately 4.8 (Mn to pH of 7) and dilute to 150 ml with water. Add one drop of calcein (0.1% in 0.001*N* NaOH) and back titrate with a standard copper solution to the quenching of the fluorescence of the free indicator. The titrations should be carried out with ultraviolet light as the sole source of illumination.

DISCUSSION

The columns used for this work were constructed from a 1-cm diameter filter tube with a coarse frit. One end was flared and attached to one inch pyrex tubing three inches long so as to leave an eight inch section of tubing (resin bed), 1 cm in diameter between the frit and the large tubing. The tubing on the other side of the frit was reduced and attached to a 2-mm capillary stopcock. The stopcock was placed as close to the frit as possible. During the elutions the flow rate is controlled by the stopcock so as to allow one drop of solution every 4–6 sec.

The determination of cobalt and iron using EDTA is carried out most conveniently using calcein as an indicator and a standard copper solution as a back titrant. The determination of 50 mg of cobalt or iron in 150 ml of solution by this method presents no difficulty. Conventional indicators may be used but a smaller aliquot must be taken with a resultant larger error in the determination.

The iron, vanadium and manganese may be easily determined by other methods. However, the procedure developed for the cobalt determination also provides a convenient separation and determination of the other elements in these alloys.

SUMMARY

A convenient ion exchange separation particularly designed for the separation of iron and vanadium or mangenese from cobalt has been developed for the determination of iron, cobalt and manganese or vanadium in soft magnetic alloys. After an anion exchange separation of their chloride complexes these elements are determined by a back titration of an excess of EDTA with a standard copper solution using calcein as an indicator under ultraviolet light.

RÉSUMÉ

Une méthode de séparation par échange d'ions est proposée pour le dosage du fer et du cobalt, accompagnés de manganèse ou de vanadium. Après séparation, ces éléments sont dosés par titrage au moyen de l'acide éthylènediaminotétracétique en excès que l'on détermine avec une solution de cuivre étalon, en présence de calcéine comme indicateur.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von Eisen, Kobalt und Mangan oder Vanadium nach vorhergehender Trennung des Eisens und Vanadiums oder Mangans vom Kobalt mit Hilfe von Ionenaustauschern. Nach der Trennung werden diese Elemente durch Rücktitration eines zugesetzten Überschusses von Äthylendiamintetraessigsäure mit einer Standard-Kupfersalzlösung in Gegenwart von Calcein als Indikator bestimmt.

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DETERMINATION OF URANIUM IN ZIRCON*

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INTRODUCTION

One of the methods of measuring geologic time involves the quantitative determination of lead and uranium. The value of this method depends on both the accuracy and precision with which both lead and uranium can be determined.

In igneous rocks, the uranium and thorium content is generally higher in the accessory minerals than in the major rock forming minerals. Of the common accessory minerals, zircon usually has the highest uranium content, approximately 0.1%. The determination of uranium in zirconium minerals such as zircon is difficult by classical methods, especially if the sample is small. The extraction-fluorimetric method was adopted as the basis for analysis. The uranium is separated from interfering elements before preparation of the fluoride phosphor. This separation usually involves the solvent extraction or uranyl nitrate from HNO_3 solution after the addition of a salting agent. A portion of the solvent is then transferred to the standard container and after evaporation of the solvent, the phosphor is prepared. Vanadium, cerium(IV), thorium, and zirconium which are partly extracted cause quenching, especially if the ratios of these elements to uranium are large. This serious quenching effect of zirconium on the fluorescence of uranium is very pronounced in the intermediate-concentration (about 1000 p.p.m.) or low-concentration (about 100 p.p.m.) ranges.

Several investigators[1-3] have inhibited the extraction of zirconium from chromatographic columns by use of a number of anions, for example, phosphate, sulfate, oxalate, or tartrate as complexing agents. Precipitation with phosphate in high acid medium is a standard procedure for the separation of zirconium from other elements.

The purpose of this study was to obtain formal data on the effectiveness of phosphate as a retainer for zirconium in the extraction process and to develop a simple method for the determination of as little as 0.0005% of uranium in zircons.

Interference by zirconium

The effect of varying amounts of zirconium on the fluorescences obtained for phosphors containing a known concentration of uranium is shown in Fig. 1. The effect of similar amounts of zirconium in the extraction method is shown in Fig. 2. Each reading is the average of replicate independent determinations. The data (Fig. 2) show that at a zirconium concentration around 10 μg/5 ml, sufficient zirconium is carried into the ethyl acetate phase to cause about 5% quenching of the uranium fluorescence. The interference by zirconium approaches a limiting value when the sample solutions contain more than 500 μg zirconium per 5 ml.

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* Publication authorized by the Director, U. S. Geological Survey.

Effect of phosphate concentration on uranium extraction

The effect of phosphate concentration in absence of zirconium was first investigated. Solutions containing two levels of uranium and varying amounts of Na_2HPO_4 ranging from 0 to 100 mg were prepared in duplicate and processed through the extraction procedure. The data obtained from phosphors containing 0.12 μg and 0.30 μg U, respectively, are presented in Table I. The results show that as much as 100 mg of phosphate does not interfere in the extraction of uranyl nitrate with ethyl acetate. Plots of data, relating fluorescence to the uranium content, obtained with and without phosphate being present during the solvent extraction of uranyl nitrate, resulted in identical curves.

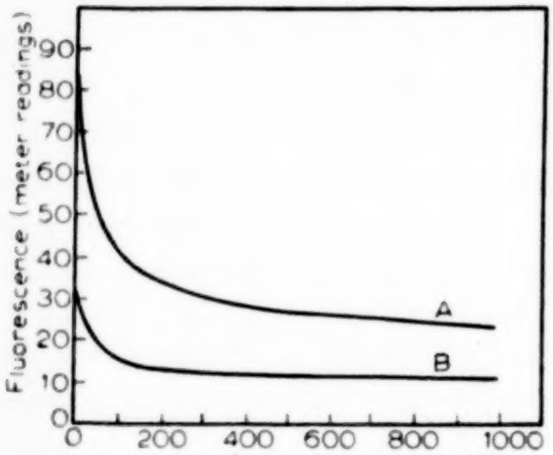

Fig. 1. The effect of zirconium upon the fluorescence of uranium-activated phosphor. Curve A, 0.3 μg U in phosphor. Curve B, 0.1 μg U in phosphor.

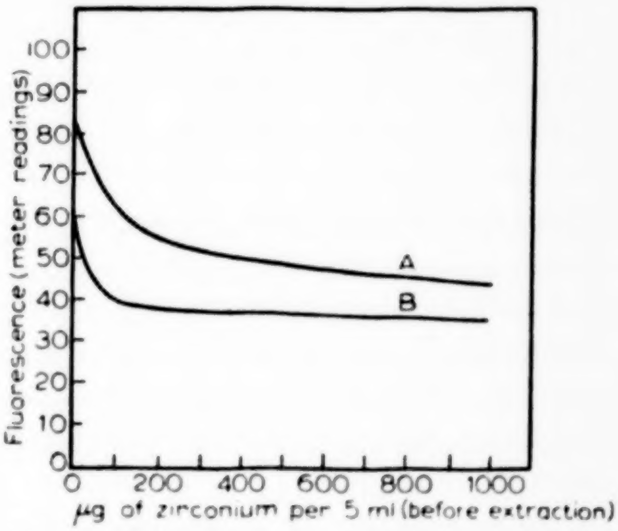

Fig. 2. The effect of zirconium upon the fluorescence of uranium-activated phosphor in the extraction method. Curve A, 0.3 μg U in phosphor. Curve B, 0.2 μg U in phosphor.

TABLE I

THE EFFECT OF VARYING AMOUNTS OF PHOSPHATE UPON THE SOLVENT EXTRACTION OF URANYL NITRATE

Phosphate (mg)	*Fluorescence (meter readings)* *0.12 µg U in phosphor*	*Fluorescence (meter readings)* *0.30 µg U in phosphor*
none	45, 45	90, 89
10	45, 45	90, 88
20	46, 46	89, 88
40	45, 45	90, 88
60	45, 45	90, 88
80	46, 46	89, 89
100	46, 45	90, 90

Separation of uranium from zirconium

The presence of large amounts of zirconium is a major interference because of its partial extraction. Therefore, the extent of retention of zirconium by phosphate was investigated. Table II shows the fluorescence readings obtained for two series of solutions prepared in duplicate containing a known concentration of uranium (0.6 μg and 1.5 μg U, respectively), 50 mg Na_2HPO_4, and amounts of zirconium varying

TABLE II

SEPARATION OF URANIUM FROM ZIRCONIUM IN PRESENCE OF PHOSPHATE

Zirconium (μg)	*Fluorescence (meter readings)*	
	0.6 μg U in solution being extracted, 0.12 μg U in phosphor	*1.5 μg U in solution being extracted, 0.3 μg U in phosphor*
none	43, 44	91, 91
10	43, 44	91, 91
50	44, 43	92, 92
100	43, 43	92, 92
200	44, 44	91, 90
500	44, 44	90, 91
1000	43, 44	90, 91

up to 1 mg. The fluorescence readings show no significant change due to the presence of zirconium in the original solution. Additional studies made to determine the amount of zirconium retained in the aqueous phase by 50 mg Na_2HPO_4 during the solvent extraction showed that as much as 10 mg of zirconium was effectively retained. The order of addition of Na_2HPO_4 is important. Low recoveries of U resulted when the phosphate was added before the saturation of the sample solution with aluminum nitrate.

The data (Table II) also indicate that the recovery of uranium and its separation from zirconium is quantitative. Further tests showed that as little as 0.1 μg of uranium was quantitatively separated from 10 mg of zirconium (approximately a 1:100,000 U:Zr ratio).

PROCEDURE

Grind the sample to an impalpable powder in a boron carbide mortar and mix thoroughly. Small particle size is necessary to insure complete fusion in a reasonable time. Weigh 0.1000 g sample into a 15-ml platinum crucible and add 1 g of carbonate-borate flux prepared by mixing equal portions by weight of anhydrous sodium carbonate and anhydrous sodium borate[4]. Mix thoroughly. Cover the crucible and place in a heated (150°–200°) furnace to drive off any moisture. Gradually increase the temperature until the mass is a viscous liquid (approximately 950°). Keep the crucible at this temperature for 20 to 30 min. Cool to room temperature and place the crucible and melt in a 100-ml beaker, add 15 ml (3+7) HNO_3, cover, and digest on a steam bath until the melt just dissolves. Transfer the solution quantitatively to a 50-ml volumetric flask removing and washing the crucible. Adjust the volume to 50 ml with water. The final nitric acid concentration is 7% v/v.

Place a 5-ml aliquot of sample solution in a 30-ml glass-stoppered test tube containing 9.5 g of low-uranium $Al(NO_3)_3 \cdot 9H_2O$. Place the tubes in a hot-water bath, and shake occasionally until solution is complete. Add 50 mg of solid Na_2HPO_4 and replace stoppered test tube in the hot-water bath in order to dissolve the phosphate. When solution is complete, cool the solution to room temperature or below.

Add 10 ml of ethyl acetate to the sample solution and transfer the stoppered test tubes together with rack to an automatic shaker, and then agitate for 5 min. Allow the phases to separate and carefully decant the supernatant ethyl acetate phase through a dry, dense, "ash-free" paper self-supported in the neck of a glass-stoppered test tube, thus removing any entrained water phase.

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Pipette off a 2-ml aliquot of the filtrate and transfer to a special platinum dish[5] that is partly immersed in cold water. To prevent loss by creeping, immediately ignite the ethyl acetate by means of a small flame and allow the solvent to burn off. Then, heat the dishes on a hot plate or under an infra-red lamp at slightly above 100° until the residual liquid is evaporated.

Use the "fused" flux recommended by GRIMALDI, MAY, AND FLETCHER[5] containing 9% NaF, 45.5% Na_2CO_3, and 45.5% K_2CO_3 by weight. It has been found satisfactory for the measurement of fluorescence obtained from less than 10^{-8} g of uranium, and yields reproducible blanks at high instrumental sensitivity. Add 2 g of flux to each dish and place the dish in a dessicator until ready for fusion. Fusions are carried out in an apparatus[6] devised for preparing phosphors. The apparatus prepares 18 phosphors at a time and eliminates the tedious and time-consuming hand operation, while improving precision. Heat the samples for 8 min which is about 6 min longer then the melting time.

Cool the dishes on the apparatus for 10 min. Then, remove and place in a dessicator where they cool for 20 min before reading. Determine the fluorescence of the button using a reflection fluorimeter[5] if the sample contains more than 0.01% U and using a Model VI transmission fluorimeter[7] if the sample contains less than 0.01% U. Obtain the uranium content of each button by comparison of its fluorescent intensity with that from buttons obtained from known solutions cycled through the modified procedure.

RELIABILITY OF RESULTS

A series of synthetic samples were prepared to obtain reproducibility data for the procedure. The results of these tests are presented in Table III. Results of analyses have an accuracy of 97–98% of the contained uranium and a standard deviation of less than 2.5%. Samples of zircon were also analyzed using the original fluorimetric method and the modified procedure. The comparative data (Table IV) show that low results are obtained when the phosphate retainer is omitted from the procedure.

TABLE III

RELIABILITY OF RESULTS (0.12 μg U)

μg Uranium found (extracted in presence of 5 mg Zr)	*μg Uranium found (extracted in presence of 10 mg Zr)*
0.118	0.118
0.118	0.124
0.124	0.126
0.124	0.126
0.120	0.120
0.118	0.120
0.118	0.120
0.120	0.120
0.118	0.120
0.120	0.120
0.118	0.126
0.120	0.120
Average = 0.1196	Average = 0.1220
Standard deviation = 0.0021	Standard deviation = 0.0028
% Standard deviation = 1.8	% Standard deviation = 2.3

TABLE IV

ANALYSIS OF ZIRCON

Zircon	*Uranium content (p.p.m.)*	
	without phosphate	*with phosphate*
Original SS-S-487-8[a]	430	550
Leached SS-S-487-8[a]	330	420
Original SS-S-487-9[a]	105	123
Leached SS-S-487-9[a]	78	93
120-BNH-36[b]	2430 ± 10	2610 ± 10
198-BNH-72[b]	2390 ± 10	2590 ± 10
189-BNH-64[b]	7730 ± 10	7880 ± 10

[a] Analyses by ALICE CAEMMERER, U. S. Geological Survey, Wash., D. C.
[b] Analyses by MARIAN SCHNEPFE, U. S. Geological Survey, Wash., D. C.

CONCLUSIONS

Routine fluorimetric analyses for uranium in zircons can be accomplished rapidly and accurately using Na_2HPO_4 as a retainer for zirconium. The standard deviation obtained from routine replicate analyses performed in this manner is less than 2.5% when uranyl nitrate is solvent-extracted in the presence of approximately 100,000 times the amount zirconium. The conditions described in the modified procedure have proved valuable in the separation of μg amounts of uranium from large amounts of zirconium.

ACKNOWLEDGEMENT

This work is part of a program being conducted by the U. S. Geological Survey on behalf of the Division of Research of the U. S. Atomic Energy Commission.

SUMMARY

A routine fluorimetric procedure is described for the determination of trace amounts of uranium in zircon. It employs the direct extraction of uranyl nitrate with ethyl acetate using phosphate as a retainer for zirconium. Submicrogram amounts or uranium are separated in the presence of 100,000 times the amount of zirconium. The modified procedure has been worked out using synthetic mixtures of known composition and zircon. Results of analyses have an accuracy of 97–98% of the contained uranium and a standard deviation of less than 2.5%.

RÉSUMÉ

Une méthode fluorimétrique est proposée pour le dosage de traces d'uranium dans un zircon. On procède à l'extraction directe du nitrate d'uranyle, au moyen d'acétate d'éthyle.

ZUSAMMENFASSUNG

Es wird eine fluorimetrische Methode zur Bestimmung von Spuren von Uran in Zirkonium beschrieben. Sie beruht auf einer direkten Extraktion von Uranylnitrat mit Äthylacetat.

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SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF COBALT, NICKEL AND COPPER WITH N,N'-BIS(3-DIMETHYLAMINOPROPYL)DITHIO-OXAMIDE

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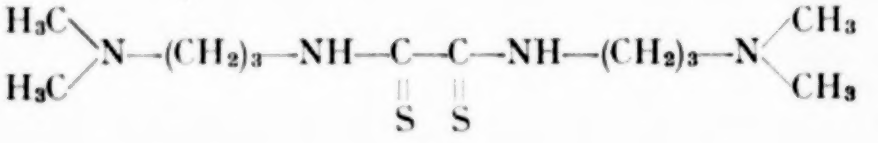
INTRODUCTION

In a recent study of a series of substituted dithio-oxamides[1] it was found that one derivative, N,N'-bis(3-dimethylaminopropyl)dithio-oxamide, showed promise of being a good reagent for the simultaneous spectrophotometric determination of cobalt, nickel and copper. This reagent has been investigated fully to see if it has any advantages over dithio-oxamide (rubeanic acid)[2] as a reagent for these three metal ions.

N,N'-bis(3-dimethylaminopropyl)dithio-oxamide has the following structure:



$$\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>N-(CH_2)_3-NH-\underset{\overset{\|}{S}}{C}-\underset{\overset{\|}{S}}{C}-NH-(CH_2)_3-N<\!\!\begin{matrix}CH_3\\CH_3\end{matrix}$$

I

The same dissociation and tautomerism equilibria may be postulated for this compound as was done in the case of dithio-oxamide. A high concentration of the active anionic form of the reagent is achieved by removal of H^+ ions, *i.e.*, by the addition of hydroxide ions.

Compound I is subject to fewer interfering ions than is dithio-oxamide and the effect of the nickel to cobalt ratio is not as great a factor in the determination as is the case in the dithio-oxamide procedure.

The sensitivities of the cobalt and copper color reactions of Compound I are comparable to the respective reactions with dithio-oxamide. The sensitivity of the nickel reaction with the reagent is about 10% less than the corresponding reaction with dithio-oxamide.

APPARATUS

Spectrophotometers

Beckman spectrophotometers, Model DK-2 and Model DU, with matched 1-cm Corex cells were used.

pH Meter

A Beckman pH meter, Model G, was employed for all pH measurements. It was calibrated with Fisher certified standard buffers.

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REAGENTS

Standard cobalt solution

A solution containing 1 mg cobalt/ml was prepared by dissolving 2.03 g of cobalt chloride hexahydrate in doubly-distilled water. Twice distilled hydrochloric acid was added so that the final concentration, after dilution to 500 ml, was one molar. The solution was standardized electrolytically.

Standard nickel solution

A standard nickel solution containing 1 mg nickel/ml was prepared by dissolving 2.03 g of nickel chloride hexahydrate in the above manner. The solution was standardized by the dimethylglyoxime gravimetric method.

Standard copper solution

A copper solution containing 1 mg copper/ml was prepared by dissolving 1.45 g of cupric chloride dihydrate in the above manner. The solution was standardized electrolytically.

Buffer solutions

A pH-9 buffer was prepared by dissolving 3.84 g of sodium borate decahydrate in 1 l of doubly-distilled water and a pH-4 buffer by dissolving 1.01 g of potassium acid phthalate in 100 ml of doubly-distilled water. All other buffers were prepared according to the directions given by BRITTON[3].

N,N'-bis(3-dimethylaminopropyl)dithio-oxamide solution

A $1.5 \cdot 10^{-3} M$ solution of this reagent was prepared by dissolving 43.5 mg in 100 ml of 95% ethanol.

Gum acacia solution

A 0.1% solution of gum acacia was prepared by dissolving 0.2 g in 200 ml of doubly-distilled water.

Doubly-distilled water

All water used in this work was distilled twice and finally run through a cation-exchange resin, Amberlite IR-120. The resin column was 26 cm in length and had an internal diameter of 2 cm.

Other reagents

All other reagents were analytical grade and were used without further purification.

EXPERIMENTAL

Properties of the reagent

N,N'-bis(3-dimethylaminopropyl)dithio-oxamide is a yellow solid which is more soluble in ethanol than the parent compound. An ethanolic solution of the reagent is pale yellow. The absorbance curve of a $1.2 \cdot 10^{-4} M$ solution is shown in Fig. 1. In practice a $1.5 \cdot 10^{-3} M$ reagent solution is employed so that the useful range of metal ion concentrations may conveniently be used and still have a sufficient excess of reagent.

The reagent solution is stable to light, hydrolysis, and oxygen and carbon dioxide of the air for at least a month. Absorbance measurements on the reagent solution showed no significant change over this period; measurements were not made over a longer time.

Properties of the complexes

Color. Cobalt, nickel and copper form water-insoluble complex salts with the reagent solution. The cobalt complex is yellow, the nickel complex reddish orange and the copper complex olive green. A protective colloid keeps the complexes in solution over the concentration range used. Gum acacia and gelatin are the substances generally used for this purpose. Gelatin solutions are stable for about a week, whereas gum acacia solutions a month old were just as effective in keeping the complexes in solution as ones freshly prepared. Consequently, gum acacia was the protective colloid used in this work. Absorbance curves of 2.00 p.p.m. solutions of the complexes are shown in Fig. 1. The absorbances of the complexes were measured against a reagent blank. The nickel and copper complexes have a maximum at 500 mμ and 365 mμ, respectively, while the cobalt complex has a broad adsorbance peak with the maximum occurring at 350 mμ. At 430 mμ the sensitivity of the cobalt reaction is about 2% less than at 350 mμ. Since the absorbance due to the reagent, the nickel and copper complexes are less at 430 mμ than at 350 mμ, the former is the most advantageous wavelength to use when simultaneous determinations are to be made.

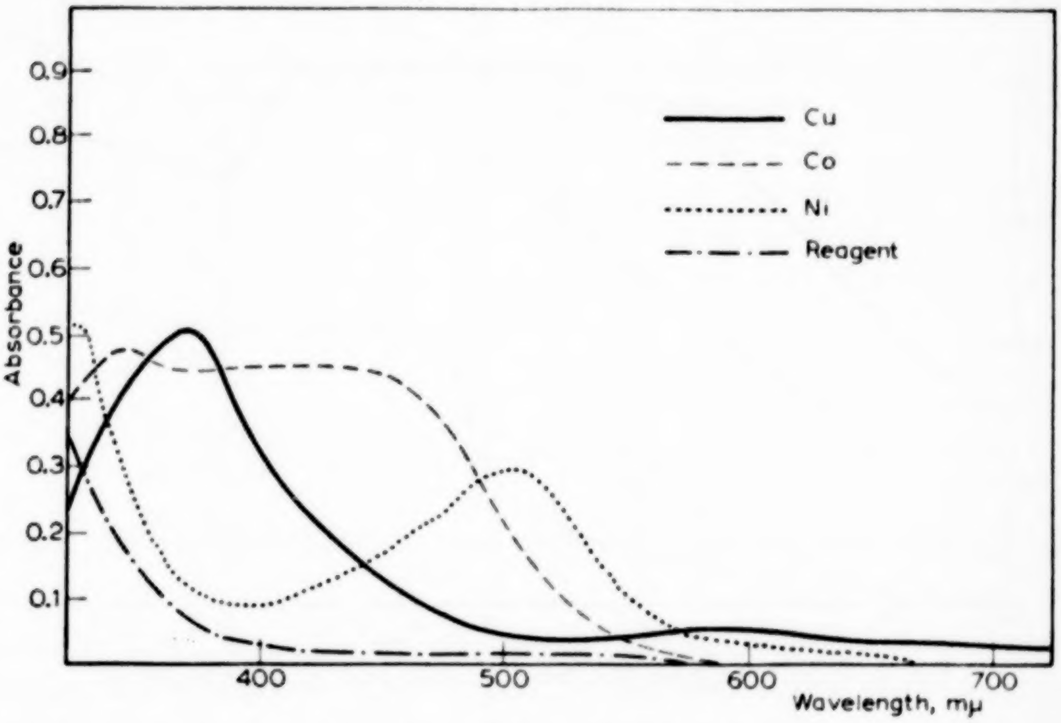


Fig. 1. Absorbance curves of 2.00 p.p.m. solutions of the cobalt, nickel and copper complexes. Reagent curve, $1.2 \cdot 10^{-4}M$. All at pH 9.

Effect of pH. The effect of the hydrogen-ion concentration is shown in Fig. 2. The absorbance curves were obtained by using 1.60 p.p.m. of the ion, 4 ml of a 0.1% gum acacia solution, 10 ml of a buffer solution of the desired pH and 3 ml of the reagent solution. The samples were diluted to 25 ml with distilled water and absorbance measurements made against a reagent blank. From the curves it is seen that the optimum pH for making simultaneous measurements is 9.0 ± 0.3.

Rate of color formation. The cobalt and nickel complexes require 30 min for maximum color development at 20°. The rate of color formation was found to vary from 35 min at 15° to 20 min at 35°. The copper complex on the other hand exhibits maximum color development at once. Temperature studies made at 15°, 20°, and 35° on the copper complex showed the absorbance to be at a maximum when the first measurement was made. Since the rate of reaction in the case of the cobalt and nickel complexes was not greatly increased at 35°, all determinations were made at room temperature and the color allowed to develop for 30 min.

Structure of the complexes in solution. The empirical formulas of the three complexes *in solution* were established by the mole ratio method of YOE AND JONES[4] and the continuous variations method of JOB[5] as modified by VOSBURG AND COOPER[6]. The results of these two methods applied to the cobalt complex are shown in Figs. 3 and 4. They indicate a ratio of 2 moles of cobalt to 3 moles of reagent. This corresponds to a salt of Co^{+3} and reagent having the formula:

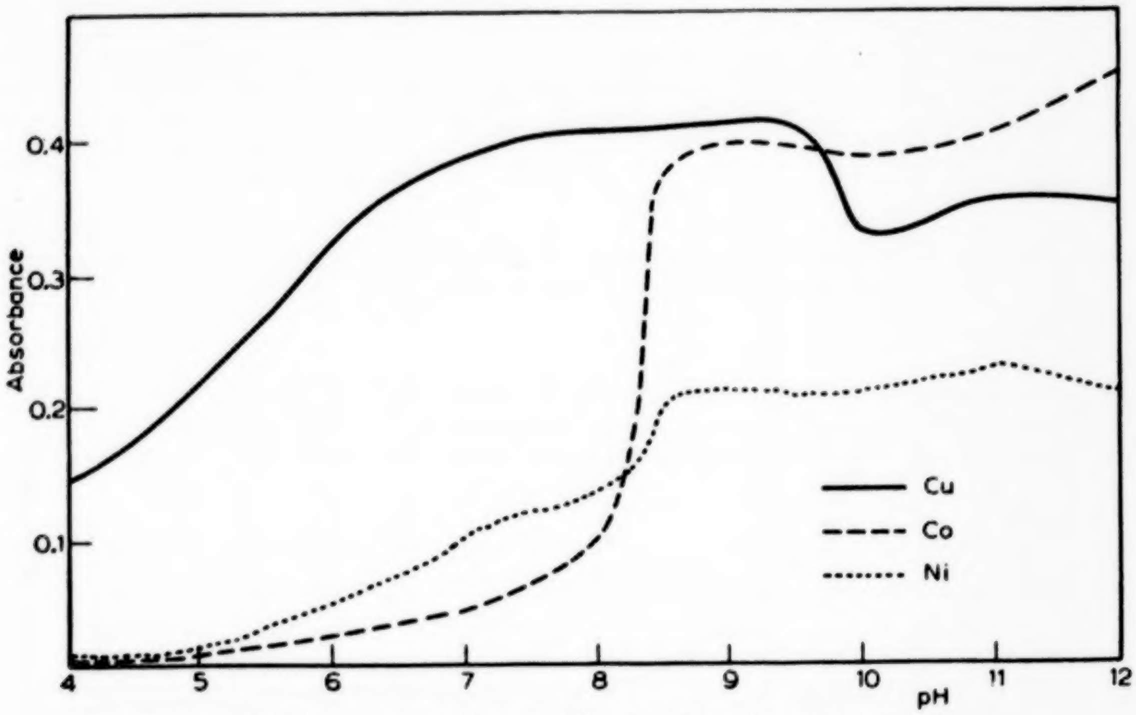


Fig. 2. Effect of pH on the cobalt, nickel and copper complexes.

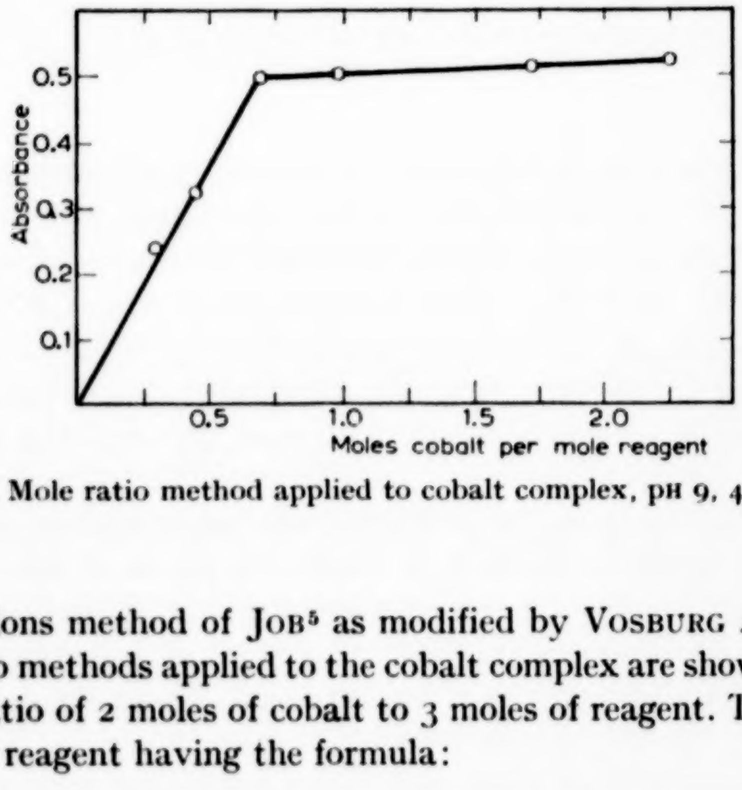
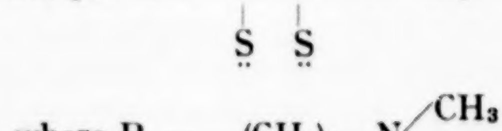
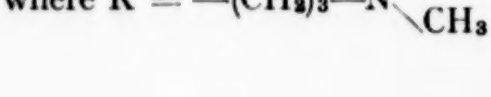


Fig. 3. Mole ratio method applied to cobalt complex, pH 9, 430 mμ.



$$\mathrm{Co_2}\,[\mathrm{R{-}N{=}}\underset{\substack{|\\ \underset{\cdot\cdot}{\mathrm{S}}}}{\mathrm{C}}{-}\underset{\substack{|\\ \underset{\cdot\cdot}{\mathrm{S}}}}{\mathrm{C}}\mathrm{{=}N{-}R}]_3$$



$$\text{where } \mathrm{R} = {-}(\mathrm{CH_2})_3{-}\mathrm{N}\begin{matrix}\diagup\mathrm{CH_3}\\ \diagdown\mathrm{CH_3}\end{matrix}$$

Nickel and copper each combine in ratios of one mole ion to one mole reagent, indicating that salts are formed by Ni^{+2} and Cu^{+2} reacting with the divalent N,N'-bis-(3-dimethylaminopropyl)dithio-oxamate anion.

Order of addition of reagents. The solutions containing the metallic ion and protective colloid must be adjusted to the proper pH before addition of the reagent solution if maximum sensitivity is to be attained.

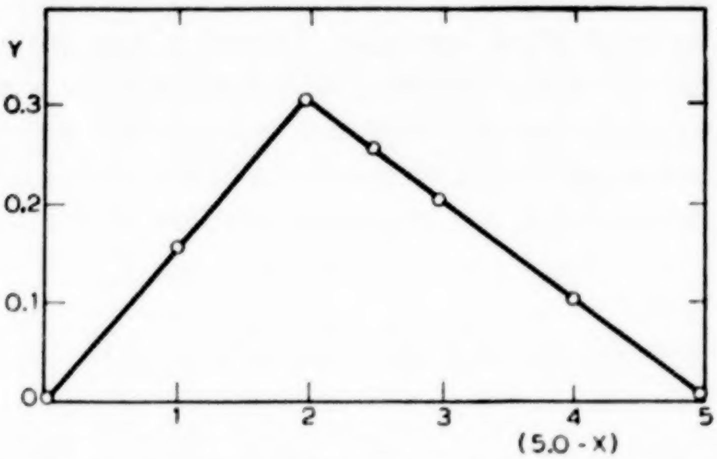


Fig. 4. Continuous variations method applied to cobalt complex, pH 9, 430 mμ.

Adherence to Beer's law. Samples containing varying concentrations of the metallic ion, 4 ml gum acacia solution, 10 ml pH 9 buffer and 3 ml reagent solution were allowed to develop for 30 min after which they were diluted to 25 ml with distilled water. The absorbances of these solutions were measured against a reagent blank at wavelengths of 430 mμ, 500 mμ and 365 mμ for the complexes of cobalt, nickel and copper, respectively. Beer's law is obeyed by all three systems over the range 0.16 p.p.m. to 4.00 p.p.m. Lower and higher concentrations were not investigated.

Effect of diverse ions. Palladium is the only ion that reacts with N,N'-bis(3-dimethylaminopropyl)dithio-oxamide in alkaline medium exclusive of cobalt, nickel and copper. It was found to produce a change in absorbance of 0.010 unit in the measurement of the cobalt complex when present in ratios of 1:1 or more. Higher tolerances may be allowed in the determination of copper and nickel but since the procedure is for the analysis of all three ions, the limiting concentration of palladium is determined by its effect on the cobalt complex.

The cyanide ion must be absent because it forms more stable complexes with cobalt, nickel and copper than does the reagent. High concentrations of citrate and tartrate ions, *i.e.*, concentrations high enough to prevent the precipitation of iron and aluminum at pH 9, interfere in the determination of all three ions.

Ions such as Fe^{+3}, Al^{+3}, Mn^{+2}, etc. which precipitate in alkaline solution must be absent, or, if present, must either be removed or complexed to prevent their interference.

Sensitivity. The sensitivities of the color reactions as defined by SANDELL[7] are as follows:

for cobalt at 430 mμ, 0.0045 γ/cm^2
for nickel at 500 mμ, 0.0077 γ/cm^2
for copper at 365 mμ, 0.0039 γ/cm^2.

Practical sensitivities based upon an absorbance of 0.005 unit are 0.025 p.p.m. cobalt, 0.039 p.p.m. nickel and 0.020 p.p.m. copper.

Simultaneous determination of cobalt, nickel and copper. Table I lists the values of the molar extinction coefficients of the complexes of cobalt, nickel and copper measured at wavelengths of 430 mμ, 500 mμ and 365 mμ, respectively. These values may be used to derive equations for the determination of one or more components[8]. The equations derived from these values are given in Table II. It was found that the presence of cobalt does not result in a shift of the absorbance peak of the nickel complex as is the case with dithio-oxamide. However, the absorbance curve of the nickel complex is altered by the presence of cobalt in such a way that the molar extinction coefficients of the nickel complex at 430 mμ and 365 mμ, respectively, are different from the values calculated on the basis of the nickel complex alone. Fig. 5 shows the absorbance curves of a 2.00 p.p.m. solution of the nickel complex alone and in the presence of 1.00 p.p.m. cobalt. Consequently, two values of the molar extinction coefficients of the nickel complex, at 430 mμ and at 365 mμ, must be considered. In Table I the values of the molar extinction coefficients of the nickel complex formed in the presence of cobalt are given in parenthesis.

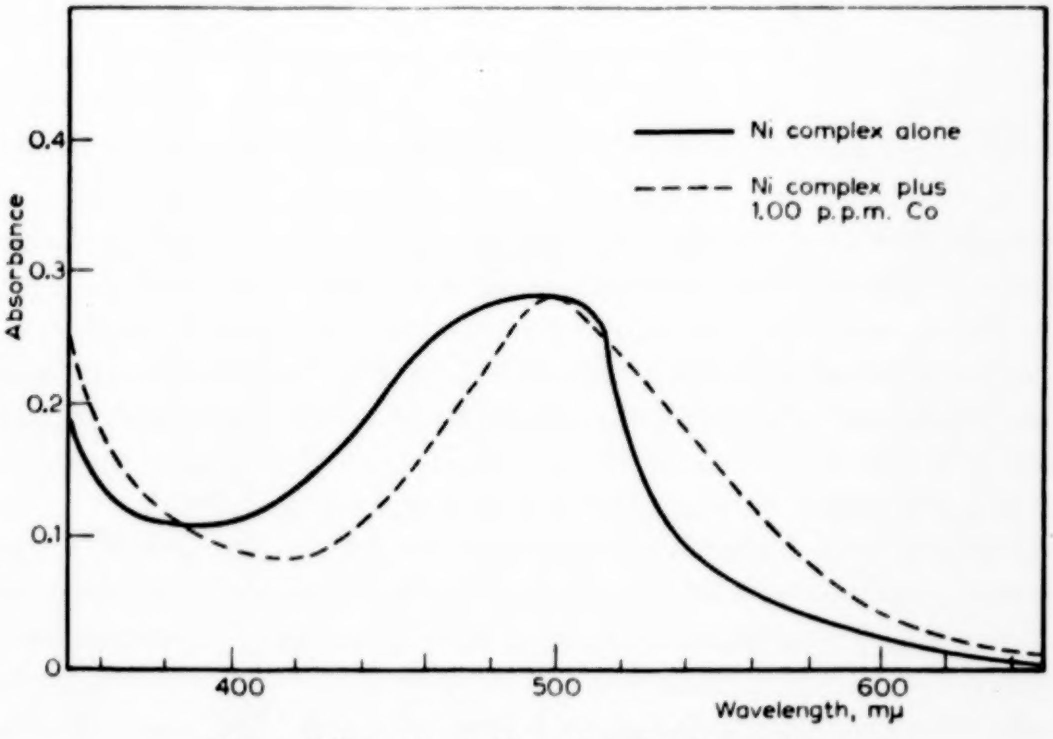


Fig. 5. Effect of cobalt on the nickel complex.

Recommended procedure. The optimum conditions for the determination of cobalt, nickel and copper are those under which the absorbances of the complexes are the highest, the most stable and the most reproducible. These conditions are fulfilled by measuring the absorbance of a solution at 500 mμ, 430 mμ, and 365 mμ respectively, against a reagent blank containing 2 ml of reagent solution, which has been prepared as follows: the complexes are formed at a pH of 9.0 ± 0.3 in the presence of 4 ml of a 0.1% gum acacia solution by adding 3 ml of a $1.5 \cdot 10^{-3} M$ reagent solution. Allow the sample 30 min for maximum color development. Dilute to 25 ml, mix and measure the absorbances at the indicated wavelengths. The molar concentrations of the ions are then calculated by using the spectrophotometric equations in Table II.

TABLE I

MOLAR EXTINCTION COEFFICIENTS OF THE COBALT, NICKEL AND COPPER COMPLEXES

Co	*365 mμ*	*430 mμ*	*500 mμ*
εCo	14,000	14,500	6,450
εNi	3,140 (4,700)	4,070 (2,640)	7,150
εCu	15,000	4,580	1,970

TABLE II

SPECTROPHOTOMETRIC EQUATIONS

One of three ions present
$(\mathrm{Co})\cdot 10^5 = 6.89\ A_s\ 430$
$(\mathrm{Ni})\cdot 10^5 = 14.0\ A_s\ 500$
$(\mathrm{Cu})\cdot 10^5 = 6.67\ A_s\ 365$
Two of three ions present
$(\mathrm{Co})\cdot 10^5 = 8.03\ A_s\ 430 - 2.63\ A_s\ 500$
$(\mathrm{Ni})\cdot 10^5 = 16.3\ A_s\ 500 - 7.25\ A_s\ 430$
$(\mathrm{Co})\cdot 10^5 = 9.75\ A_s\ 430 - 2.97\ A_s\ 365$
$(\mathrm{Cu})\cdot 10^5 = 9.42\ A_s\ 365 - 9.08\ A_s\ 430$
$(\mathrm{Ni})\cdot 10^5 = 14.8\ A_s\ 500 - 1.95\ A_s\ 365$
$(\mathrm{Cu})\cdot 10^5 = 7.08\ A_s\ 365 - 3.10\ A_s\ 500$
Three ions present
$(\mathrm{Co})\cdot 10^5 = 10.6\ A_s\ 430 - 2.99\ A_s\ 365 - 1.95\ A_s\ 500$
$(\mathrm{Ni})\cdot 10^5 = 16.6\ A_s\ 500 - 7.50\ A_s\ 430 + 0.11\ A_s\ 365$
$(\mathrm{Cu})\cdot 10^5 = 9.03\ A_s\ 365 - 7.46\ A_s\ 430 - 3.37\ A_s\ 500$

Analysis of synthetic samples and NBS standard samples. A series of synthetic samples and three National Bureau of Standards samples were analysed by the above procedure. Each sample had the indicated ion concentration, 4 ml of a 0.1% gum acacia solution, 3 drops of a 0.1% thymolphthalein solution and was adjusted to a pH 9.0 ± 0.3 with sodium hydroxide and hydrochloric acid until the blue color of the indicator just turned colorless. Ammonium hydroxide must not be used because the presence of high concentrations of ammonium ions prevent the development of the nickel complex. 3 ml of a $1.5 \cdot 10^{-3} M$ reagent was added and the samples given 30 min for maximum color development. The samples were diluted to the mark in 25-ml volumetric flasks, mixed and the absorbances measured at the respective wavelengths against a reagent blank which contained 2 ml of reagent solution. The results are given in Tables III and IV.

In order to prevent precipitation of the hydrated oxides of aluminum and iron when the NBS samples 85a, 87 and 58 were analysed, the aluminum was complexed

TABLE III

ANALYSIS OF SYNTHETIC SAMPLES

Sample	*Added (p.p.m.)*	*Found (p.p.m.)*
1	Ni 1.00	1.08
	Cu 2.50	2.52
2	Ni 1.70	1.72
	Cu 1.50	1.51
3	Ni 2.35	2.34
	Cu 1.00	1.09
4	Co 2.50	2.47
	Cu 1.00	0.98
5	Co 1.50	1.36
	Cu 1.70	1.62
6	Co 1.00	1.08
	Cu 2.30	2.37
7	Co 0.90	0.94
	Ni 2.50	2.45
8	Co 1.40	1.37
	Ni 1.30	1.33
9	Co 2.50	2.30
	Ni 0.80	0.92
10	Co 1.00	0.89
	Ni 2.00	1.97
	Cu 0.80	0.84
11	Co 0.50	0.48
	Ni 1.50	1.55
	Cu 1.60	1.55
12	Co 2.00	1.92
	Ni 0.50	0.39
	Cu 1.20	1.29
13	Co 0.40	0.37
	Ni 0.80	0.86
	Cu 2.50	2.54

TABLE IV

ANALYSIS OF NATIONAL BUREAU OF STANDARDS SAMPLES

Material	*NBS Value* %	*Found*	
		% Ni	*% Cu*
Al alloy, 85a	Ni 0.41	0.44	2.41
	Cu 2.48	0.38	2.50
		0.40	2.43
		0.35	2.38
	av.	0.39	2.43

TABLE IV (Continued)

Material	*NBS Value* %		*Found*	
			% Ni	*% Cu*
Al–Si alloy, 87	Ni 0.59		0.53	0.28
	Cu 0.30		0.55	0.31
			0.56	0.29
			0.54	0.28
		av.	0.55	0.29
Fe–Si alloy, 58	Ni 0.115		0.103	0.037
	Cu 0.04		0.105	0.033
			0.108	0.035
			0.105	0.038
		av.	0.105	0.036

with 5 ml of a 5%-sodium fluoride solution in the case of aluminum alloys 85a and 87 and the iron in the ferro-silicon alloy 58 was extracted with diethyl ether from a 20% hydrochloric acid solution.

ACKNOWLEDGEMENT

The authors wish to express their thanks to the Mallinckrodt Chemical Works for their gift of the N,N′-bis(3-dimethylaminopropyl)dithio-oxamide used in this work.

SUMMARY

The cobalt, nickel and copper complexes of N,N′-bis(3-dimethylaminopropyl)dithio-oxamide have been characterized in terms of color, effect of pH, rate of color formation, structure *in solution*, order of addition of reagents, adherence to Beer's law, and sensitivity. The reactivity of the reagent to other ions has been reported. A method for the simultaneous spectrophotometric determination of cobalt, nickel and copper has been developed. The results of the application of this procedure to synthetic samples and to several National Bureau of Standards samples are given.

RÉSUMÉ

Les complexes du cobalt, du nickel et du cuivre avec la N,N′-bis(diméthylamino-3-propyle) dithioxamide ont été étudiés. Une méthode spectrophotométrique est proposée pour le dosage de ces trois éléments.

ZUSAMMENFASSUNG

Es werden die Komplexverbindungen von Kobalt, Nickel und Kupfer mit N,N′-bis(3-dimethyl-amino-propyl)dithiooxamid beschrieben und über eine spektrophotometrische Methode zur Bestimmung dieser drei Elemente berichtet.

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UN DOSAGE TRÈS SÉLECTIF DU NICKEL AVEC LA CYCLOHEXANEDIONEDIOXIME

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INTRODUCTION

Nous nous proposons d'établir une méthode de séparation et de dosage du nickel dans un mélange renfermant un grand nombre de cations et plus particulièrement du cobalt en très forte quantité. Ce travail comprend trois parties; l'une a pour objet la séparation du nickel des autres cations par extraction, la seconde traite du dosage du nickel par la nioxime et dans la troisième, nous proposons quelques applications.

Pour ce travail nous utiliserons le chlorure de nickel Merck ,,cobalt frei'' et la nioxime, préparée par la maison Fluka, selon la méthode RAUH *et al.*[1] dont le point de fusion est de 185°.

SÉPARATION DU NICKEL PAR EXTRACTION

(*a*) *Extraction du nickel*

Solutions utilisées. Chlorure de nickel 0.01 M, nioxime 0.01 M, solution tampon pH 7 (50 ml de KH_2PO_4 $M/5$ + 29.63 ml de NaOH $N/5$ complété à 200 ml par addition d'eau bidistillée), acide chlorhydrique 5 N.

Mode opératoire. Dans un tube à centrifuger, on introduit 2 ml de tampon, 0.5 ml d'un solvant non miscible à l'eau, on agite trois minutes, chauffe à 80° pendant 5 min, laisse refroidir à 20° et centrifuge. Trois cas peuvent se présenter: Le précipité de nickel-nioxime reste dans la solution aqueuse (phénomène indiqué dans le Tableau I

TABLEAU I

COMPORTEMENT DES COMPLEXES Fe, Co ET Ni-NIOXIME DANS DIVERS SOLVANTS ORGANIQUES

Solvants	*Fe-nioxime*	*Co-nioxime*	*Ni-nioxime*
Alcool benzylique	soluble	soluble	soluble
Cyclohexanol	insoluble	soluble	suspension
Méthylcyclohexanol	insoluble	soluble	suspension
Méthyléthylcétone	soluble	soluble	suspension
Benzène	insoluble	insoluble	suspension
Toluène	insoluble	insoluble	suspension
Cyclohexanone	insoluble	soluble	suspension
Quinoléine	soluble	soluble	soluble
Trichloréthylène	insoluble	insoluble	suspension
Cyclohexane	insoluble	insoluble	suspension
Chloroforme	insoluble	insoluble	suspension
Pentachloréthane	insoluble	insoluble	suspension
Éther	insoluble	insoluble	suspension
Alcool amylique	insoluble	insoluble	suspension
Phénol	insoluble	insoluble	soluble

sous le terme de ,,insoluble"). Le précipité se dissout dans le solvant (soluble) ou enfin le précipité passe quantitativement dans le solvant à l'état du suspension ou de précipité (suspension).

Comme le montre le Tableau I, il ne nous a pas été possible de trouver un solvant susceptible de dissoudre la nickel-nioxime seule. Une partie du fer et du cobalt sont extraits avec le nickel. On peut par contre séparer le cobalt du fer avec la cyclohexanone et le cyclohexanol. Mais il est possible de séparer le nickel du fer et du cobalt par un processus peu usuel en analyse mais qui donne, dans notre cas, d'excellents résultats. Il s'agit de faire passer quantitativement la nickel-nioxime, à l'état solide, dans la phase organique. On obtient celle-ci soit en suspension, soit sous forme d'un précipité qui se rassemble à la surface de séparation des deux liquides mais quantitativement dans la phase organique. Les deux autres cations restent dans l'eau à l'état dissous ou de précipité. L'étude de ce phénomène s'est effectuée de la façon suivante On introduit 5 ml de tampon pH 7, 0.5 ml de la solution de $NiCl_2$ 0.01M et 1 ml de nioxime 0.0563M. On attend 10 min, le complexe est alors extrait par le solvant organique et la phase aqueuse séparée après centrifugation. Le solvant organique est traité par 5 ml d'une solution chlorhydrique 5N qui détruit le complexe lorsqu'on agite. Le nickel ne passe dans la solution aqueuse quantitativement. On sépare les deux liquides et on lave trois fois le solvant organique avec 5 ml d'eau distillée. Les résultats de quelques essais sont donnés dans le Tableau II.

TABLEAU II

µg Ni ajouté	*Solvant utilisé*	*µg Ni trouvé*	*Erreur en %*
292.5	Trichloréthylène	290	0.8
292.5	Toluène	291	0.8
292.5	Alcool amylique	288	1.3
292.5	Benzène	292	0.3
292.5	Cyclohexanol	291	0.8

Comme on le voit, les pertes sont de l'ordre de 1%. Le dosage colorimétrique du nickel a été fait dans la phase aqueuse par la méthode de FERGUSON ET BANKS[2].

Sélectivité et extraction. Nous indiquons, dans le Tableau IV, les cations gênants le dosage direct du nickel au pH de 3.5 (pH pour lequel le Ni-nioxime précipite encore quantitativement).

Nous avons effectué l'extraction du nickel, selon le processus indiqué ci-dessus, en prenant le benzène comme liquide extracteur, le dosage du nickel a été effectué par la méthode FERGUSON ET BANKS[2].

TABLEAU III

IONS INTERFÉRANT APRÈS EXTRACTION AU BENZÈNE

Ions interférant même en petite proportion: Pd^{+2}, Bi^{+3}, Sn^{+2}, Sb^{+3}, Hg_2^{+2}.

Ions ne gênant pas à faible concentration: Cr^{+6}, Pb^{+2}.

Les ions suivants n'interfèrent pas, même s'ils sont présents en forte proportion: Ag^+, Cd^{+2}, As^{+3}, As^{+5}, Cu^{+2}, Co^{+2}, Fe^{+2}, Fe^{+3}, Mn^{+2}, Mn^{+7}, Al^{+3}, Cr^{+3}, Zn^{+2}, Mg^{+2}, Ca^{+2}, Ba^{+2}, Sr^{+2}, Li^+, K^+, Na^+, NH_4^+, U^{+6}, Mo^{+6}.

TABLEAU IV

ORIGINE DE L'INTERFÉRENCE DUE À DIVERS IONS

Ions réagissant avec la nioxime au pH de 3.5:

Cu^{+2} ,	complexe brun jaune, soluble en milieu aqueux
Fe^{+2} ,	complexe brun rouge, soluble en milieu aqueux
Fe^{+3} ,	complexe brun foncé, soluble en milieu aqueux
Co^{+2} ,	complexe brun jaune, soluble en milieu aqueux
Bi^{+3} ,	complexe jaune, insoluble en milieu aqueux
Pd^{+2} ,	complexe jaune, insoluble en milieu aqueux
Ni^{+2} ,	complexe rouge carmin, insoluble en milieu aqueux

Ions précipitant au pH de 3.5:

Fe^{+3} ,	précipitation de l'hydroxyde brun
Bi^{+3} ,	précipitation d'un sel basique, BiOCl
Sn^{+2} ,	précipitation de l'hydroxyde
Sb^{+3} ,	précipitation d'un sel basique, SbOCl
$Hg_2{}^{+2}$,	dismutation en HgO et Hg

Ions colorant la solution aqueuse:

Cr^{+6} ,	coloration jaune de la solution
Mn^{+7} ,	coloration violette de la solution
$UO_2{}^{+2}$,	coloration jaune de la solution

Cette méthode d'extraction des ions gênant le dosage colorimétrique du nickel par la nioxime est très sélective, tout en étant rapide. Elle exige peu de manipulations, ce qui réduit les causes d'erreurs dues aux pertes de substance.

b) *Extraction du nickel dans un système refermant une très grande quantité de cobalt*

Dans ces conditions, la technique décrite ci-dessus ne convient pas, car elle est longue et onéreuse; il faut de grandes quantités de nioxime pour complexer le cobalt; d'autre part elle n'est plus quantitative lorsque celui-ci est en trop fortes proportions ($<$ 1/100). Nous proposons donc une préextraction du cobalt (qui ne doit pas nécessairement être quantitative) dans un solvant organique, au moyen du thiocyanate. Nous avons choisi tout d'abord comme solvant le mélange éther–amylol utilisé en colorimétrie. Mais pour que le nickel reste quantitativement dans la phase aqueuse au cours de l'extraction du cobalt, il est nécessaire que celle-ci soit suffisamment acide.

Or, au cours des extractions successives du cobalt, nous avons constaté une diminution très forte de l'acidité de la solution aqueuse, probablement par suite du passage de l'acide thiocyanique non dissocié dans le solvant organique. Cette augmentation de pH n'est pas favorable à la séparation, car une partie du nickel passe alors dans la phase organique avec le cobalt. Par contre, si on part d'une solution très acide, les pertes en nickel sont négligeables, mais l'extraction du cobalt est plus difficile et exige d'importantes quantités de solvant. Nous avons donc porté notre choix sur un autre solvant, l'acétate d'éthyle, qui permet d'effectuer une élimination rapide du cobalt sans perte de nickel en partant d'une solution aqueuse HCl 5*N*.

Appareillage et mode opératoire. L'extraction selon la technique habituelle n'ayant pas donné satisfaction (on observe des pertes en nickel pouvant aller jusqu'à 5%) nous avons mis au point un dispositif qui est une modification de l'appareil de KIRK[3] (Fig. 1).

Position des robinets au départ: 1 et 2 sont tournés de façon à assurer le passage de la solution de A à B, 1 étant fermé par rapport à F.

Le robinet 3 étant fermé, on tourne 4 et 5 de façon à ce que l'on puisse aspirer l'air à travers B au moyen de la trompe à vide D. 4 est fermé par rapport à C.

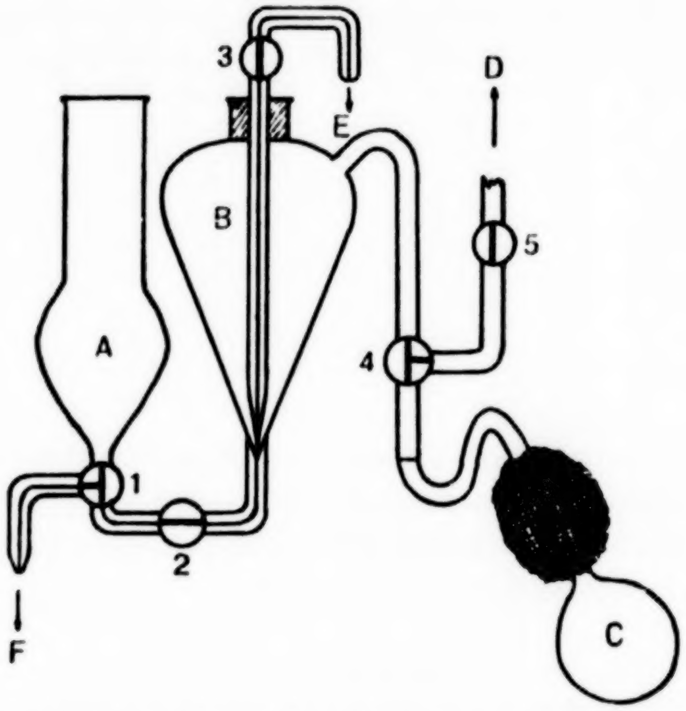

Fig. 1. Dispositif d'extraction: 1,4, robinets à 3 voies; 2, 3,5, robinets à 2 voies; A: compartiment servant au remplissage; B: compartiment d'extraction proprement dit; C: poire pour mise sous pression de B; D: à la trompe à vide; E: capillaire servant à l'élimination du solvant organique; F: capillaire permettant de récupérer la solution aqueuse.

Mode opératoire. La solution et le solvant sont introduits dans la partie A. En aspirant la solution dans B par la trompe à vide, l'air fait office d'agitateur en barbotant à travers la solution aqueuse et le solvant. Après quelques minutes, on ferme le robinet 2, coupe le vide et relie B à C au moyen du robinet 4. On met alors B sous pression au moyen de la poire C et en ouvrant 2, la solution aqueuse passe en A. Lorsque la surface de séparation des deux couches atteint l'extrémité effilée du capillaire E, on referme 2. En ouvrant 3 et en maintenant la pression dans B, le solvant est éliminé par le capillaire E. On introduit en A une nouvelle quantité de solvant et on recommence l'extraction comme ci-dessus. L'opération est terminée lorsque la solution aqueuse est incolore.

Après la dernière extraction, on fait couler la solution aqueuse par le capillaire F dans une ampoule à décanter. On lave A et B pour entraîner les dernières traces de Ni retenues aux parois. Ces eaux de lavages seront ajoutées à la solution aqueuse. L'appareil est alors prêt pour une nouvelle séparation après rinçage avec de l'eau, de l'alcool et de l'éther.

Remarques. Si le capillaire reste vide, au début des opérations d'extraction, on remarque lors de la mise sous pression de B, une légère montée de la solution aqueuse dans ce capillaire. Il faut donc, avant de commencer une séparation, remplir le capillaire E de solvant afin d'empêcher ce phénomène. Pour éviter cette montée au cours des extractions, il suffira de fermer le robinet 3 avant que l'air puisse s'introduire dans le capillaire. Les pertes en nickel au cours des extractions du cobalt sont faibles. Il a été effectué, sur des solutions de nickel à diverses concentrations, 5 extractions en utilisant pour chacune d'elles 10 ml d'acétate d'éthyle, puis le nickel restant dans la phase aqueuse a été dosé par la méthode de FERGUSON ET BANKS[2]. Les résultats sont rassemblés dans le Tableau V.

TABLEAU V

Ni théorique μg	*Ni trouvé* μg	*Ni par ml* μg	*Erreur* %
14.7	15.0	0.294	+2
29.5	28.5	0.590	—4
59.0	57.5	1.118	—3
118.0	114.0	2.360	—3
236.0	230.0	4.720	—3
295.0	288.0	5.900	—3

Bien que nous nous soyons placés dans les plus mauvaises conditions, les pertes restent légères; les 5 extractions ne sont nécessaires que si les quantités de cobalt sont considérables. Dans le Tableau suivant nous indiquons le nombre d'extractions qu'il faut faire selon la quantité de cobalt en solution.

TABLEAU VI

Co à extraire mg	*Nombre d'extractions*	*Solvant utilisé* ml
700	5	50
300	4	40
125	3	30
25	2	20

L'extraction est gênée par les ions Hg^{+2} et Hg_2^{+2} même en faibles proportions et les ions Pb^{+2} en grandes quantités.

DOSAGE COLORIMÉTRIQUE DU NICKEL PAR LA NIOXIME

La nickel-nioxime est soluble dans la quinoléine et lui confère une coloration jaune dont le coefficient d'extinction moléculaire est suffisamment grand pour rendre possible un dosage colorimétrique. La quinoléine ,,Fluka puriss" utilisée a un point d'ébullition de 236–237°. Elle est incolore. Le premier objet de cette mise au point a été d'étudier le comportement de ce solvant au spectrophotomètre.

Spectre d'absorption de la quinoléine

Nous avons constaté que celui-ci varie, pour la substance anhydre, avec le degré d'oxydation. Il dépend aussi de la quantité d'eau que renferme la quinoléine, la Fig. 2 met ce phénomène en évidence.

Pour obtenir la courbe B, nous avons introduit dans la cuve de comparaison de la quinoléine saturée d'eau bidistillée de pH 6. La littérature indique que cette substance saturée d'eau en renferme 22%, sans spécifier le pH. Avec l'eau bidistillée nous obtenons le même résultat, par contre avec de l'eau tamponnée entre les pH 2 et 10, les solubilités observées ont toujours été trouvées plus faibles; effet de sel et de pH probablement.

Pour connaître l'influence de l'eau dissoute dans la quinoléine sur le coefficient d'extinction, nous avons déterminé la densité optique D, à deux longueurs d'onde, de la quinoléine en présence de quantités variables d'eau bidistillée, comparée à la quinoléine anhydre. Les résultats sont donnés dans le Tableau VII.

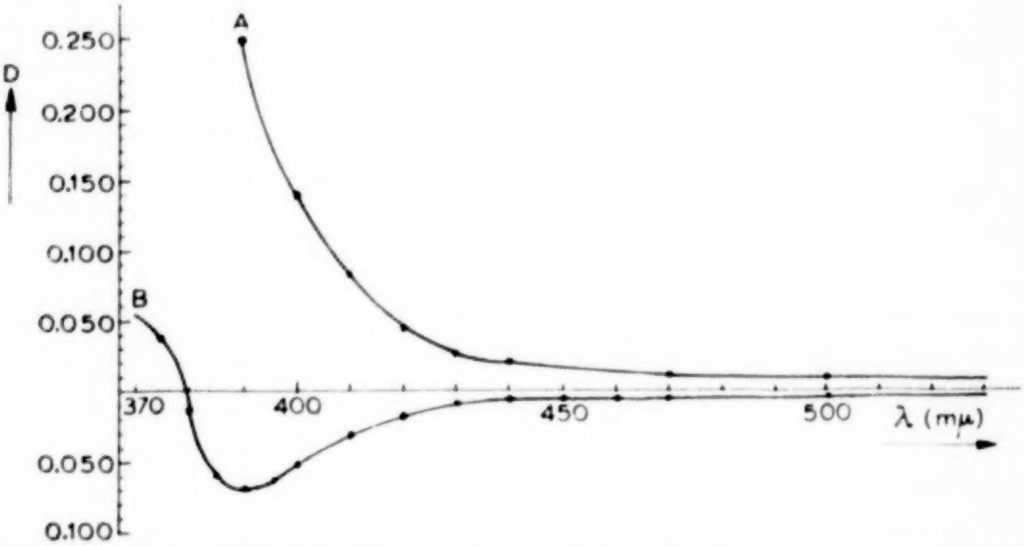

Fig. 2. Courbe A: spectre d'absorption de la quinoléine anhydre par rapport à l'eau bidistillée; Courbe B: spectre d'absorption de la quinoléine anhydre comparée à la quinoléine saturée en eau.

TABLEAU VII

Quinoléine anhydre (ml)	*Eau ajoutée (% en vol)*	*D à 436 mμ*	*D à 405 mμ*
5	5	0.005	0.035
5	10	0.006	0.042
5	20	0.003	0.056
5	22	0.004	0.056

On peut dire qu'à partir de 436 mμ et même un peu avant, la variation de la teneur en eau de la quinoléine ne modifie pas sensiblement la densité optique. Il n'en est pas de même pour des longueurs d'onde inférieures ou égales à 405 mμ.

Solubilité de la nickel-nioxime dans la quinoléine

Nous avons étudié la stabilité et la solubilité de la nickel-nioxime dans la quinoléine selon le mode opératoire donné à la p. 450. Il a été préparé six solutions renfermant des quantités croissantes de nickel dont la composition exacte est donnée ci-dessous.

La coloration s'intensifie avec la concentration en nickel. La solution VI se trouble immédiatement, la solution V le fait après 10 à 15 min, les solutions IV et III sont stables et limpides pendant 12 h seulement alors que les solutions I et II sont encore optiquement vides après trois jours. D'après les densités optiques et la courbe d'éta-

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TABLEAU VIII

Essai No	*I*	*II*	*III*	*IV*	*V*	*VI*
Phase aqueuse						
Tampon pH 5 (ml)	2.475	2.45	2.4	2.3	2.1	2.0
Nioxime 0.01M (ml)	1.5	1.5	1.5	1.5	1.5	1.5
$NiCl_2$ 0.0078M (ml)	0.025	0.050	0.1	0.2	0.4	0.5
Phase organique						
Quinoléine (ml)	2	2	2	2	2	2
Conc. en Ni (μg/ml) dans 5 ml de solvant	2.28	4.57	9.13	18.27	36.53	45.7
Après 10 min	0.060	0.115	0.225	0.430	0.855	—
Après 3 jours	0.065	0.110	0.125	0.115	0.130	—

lonnage, il a été possible d'évaluer la solubilité de la nickel-nioxime dans la quinoléine, elle est de 5 μg/ml après 3 jours et d'environ 18 μg/ml, 12 h après la mise en solution. Immédiatement après la préparation, elle est supérieure à 35/μg ml.

Spectre d'absorption de la Ni-nioxime dans la quinoléine

Les solutions sont préparées selon le mode opératoire décrit à la p. 450, 451, ce qui permet aussi d'apprécier la reproductibilité. Nous avons effectué pour chaque point 7 mesures de la densité optique dont nous donnons les valeurs extrêmes dans les colonnes 4 et 5 et la valeur moyenne dans la 2ième colonne du Tableau IX.

TABLEAU IX

λ (mμ)	*D*	ε	*D max*	*D min*
370	0.255	3100	0.280	0.230
380	0.262	3300	0.275	0.250
385	0.268	3400	—	—
390	0.263	3200	0.266	0.260
400	0.205	2500	0.207	0.204
405	0.166	2100	—	—
410	0.146	1800	0.149	0.143
420	0.117	1500	0.121	0.114
430	0.112	1400	0.113	0.111
435	0.114	1400	0.114	0.113
440	0.115	1400	0.116	0.114
445	0.116	1400	0.116	0.115
450	0.105	1300	0.106	0.104
460	0.078	1000	0.078	0.077
470	0.056	700	0.056	0.056

On peut en conclure qu'au-dessous de 430 mμ les mesures ne sont pas reproductibles. Dès que $\lambda \geqslant 430$ mμ (depuis 425 mμ même) les erreurs ne dépassent pas 2%.

Courbe d'étalonnage et dosage du nickel

Solutions utilisées. Chlorure de nickel 0.0078M, nioxime 0.01M, solution tampon pH 5 (acide acétique 0.055N + acétate de sodium 0.141M) quinoléine saturée en eau bidistillée.

Appareil. Photomètre Eppendorf, filtre 436 mμ.

Mode opératoire. On prélève, avec une micropipette de 0.2 ml, la quantité nécessaire de la solution de nickel, on l'introduit dans un tube à centrifuger de 10 ml avec 1 ml de tampon et un excès de nioxime. Après formation du précipité on ajoute 2 ml de quinoléine saturée d'eau bidistillée, on secoue pour former l'émulsion, la nickel-nioxime passe dans le solvant organique (cette opération est accélérée si on porte le mélange à env. 80°). Après refroidissement, on centrifuge et on sépare les phases. La solution de quinoléine est introduite dans un ballon jaugé de 5 ml, on complète avec une solution de quinoléine (solution utilisée préablalement pour le lavage du tube à centrifuger), puis on détermine la densité optique. Résultats: Tableau X et Fig. 4.

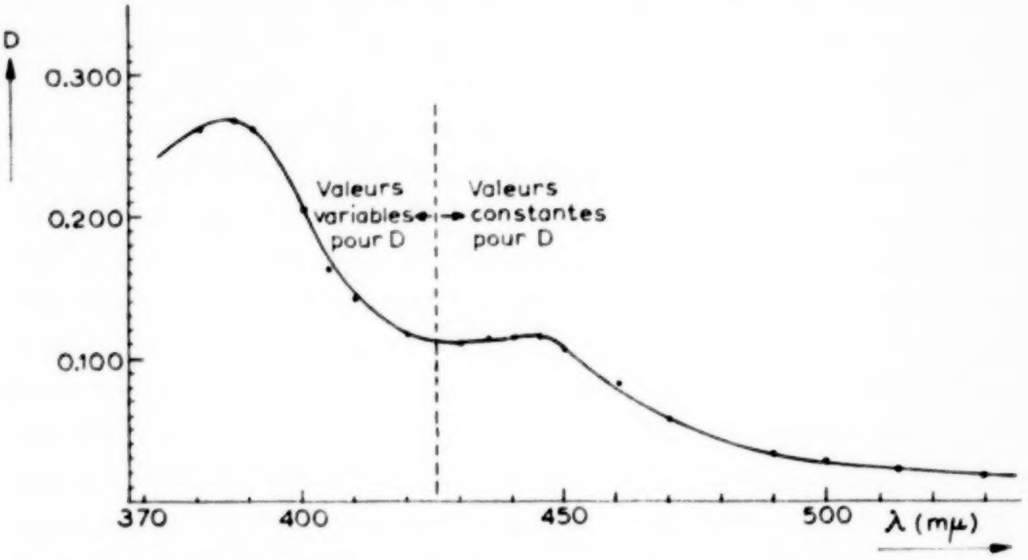

Fig. 3. Spectre d'absorption de la Ni-nioxime dissoute dans la quinoléine saturée en eau.

TABLEAU X

NiCl$_2$ ml	*Nioxime ml*	*Conc. Ni M*	*Conc. Ni μg/ml*	*D**	*ε*
0.0125	0.100	$0.194 \cdot 10^{-4}$	1.14	0.030	—
0.0250	0.100	$0.368 \cdot 10^{-4}$	2.28	0.060	—
0.0500	0.200	$0.760 \cdot 10^{-4}$	4.57	0.115	—
0.1000	0.300	$1.552 \cdot 10^{-4}$	9.13	0.225	1440
0.1500	0.500	$2.328 \cdot 10^{-4}$	13.70	0.340	1460
0.2000	0.600	$3.104 \cdot 10^{-4}$	18.27	0.430	1390
0.2500	0.800	$3.880 \cdot 10^{-4}$	22.84	0.530	1380
0.3000	0.900	$4.656 \cdot 10^{-4}$	27.40	0.645	1390
0.4000	1.200	$6.208 \cdot 10^{-4}$	36.53	0.855	1380

* Volume total de chaque solution: 5 ml.

Le coefficient d'extinction molaire est de $\varepsilon = 1420$, la coloration obéit à la loi de Beer. Il est encore possible de doser 2 μg de nickel par ml et jusqu'à 35 μg. Le photomètre Eppendorf permettant d'apprécier une variation de densité optique de 0.003, la sensibilité de la méthode est de 0.12 μg. On fait donc une erreur de 6%, erreur

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d'appareillage lorsqu'on dose 2 μg de nickel par ml. Dans le Tableau XI, nous comparons notre méthode à l'excellente méthode proposée par FERGUSON ET BANKS.

La méthode de FERGUSON ET BANKS est aussi précise que la nôtre et quatre fois plus sensible. Elle est quelque peu gênée par les variations de pH ou en présence de fortes concentrations d'électrolytes ce qui n'est pas le cas pour notre procédé. Elle est plus limitée aussi en ce qui concerne les limites de concentrations entre lesquelles le dosage est possible.

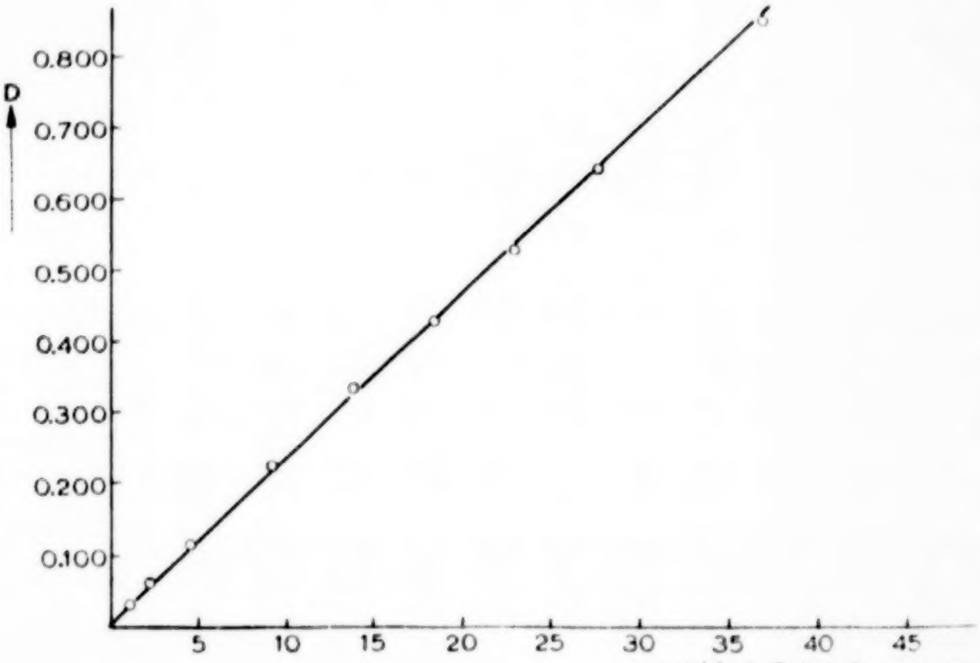

Fig. 4. Courbe d'étalonnage de la Ni-nioxime en solution dans la quinoléine saturée en eau. Cuve de comparaison: quinoléine saturée en eau; longueur d'onde: 436 mμ; longueur de la cuve: 1 cm; Concentration de la solution de base: 0.0078N.

TABLEAU XI

COMPARAISON DES DEUX MÉTHODES

Caractéristiques		*Solution dans quinoléine*	*Suspension*
Limite inférieure	:	2 μg/ml	0.5 μg/ml
Limite supérieure	:	35 μg/ml	8.0 μg/ml
Temps de stabilisation	:	10 min	30 min
Influence con. électrol.	:	aucune	légère
Influence du pH	:	aucune	légère
ε moyen	:	1412	5600

APPLICATIONS

1. *Dosage du nickel dans les sels de cobalt*

Comme nous l'avons vu, l'extraction directe de la nickel-nioxime, précipitée dans une solution aqueuse, par le benzène exige, s'il y a un grand excès de cobalt une trop grande quantité de réactif et la séparation n'est pas toujours quantitative. Nous proposons donc d'effectuer une préextraction au thiocyanate, comme il a été décrit dans la première partie. Nous préférons ce processus à celui préconisé par JOHNSON

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ET SIMMON[4], qui se basent sur une réaction proposée par FEIGL[5]. Le cobalt est oxydé en cobalti cyanure par un courant d'air, en présence d'ions cyanogène. Le complexe obtenu avec le nickel est détruit par le formaldéhyde alors que le complexe du cobalt subsiste. Ces auteurs séparent 1 partie de nickel dans 10.000 de cobalt avec une erreur de —7%. La méthode est bonne mais l'emploi du cyanure présente des inconvénients et la durée du dosage est de deux heures environ.

L'extraction au thiocyanate nous parait avantageuse, elle est plus rapide et plus effective. Pour ce faire nous utilisons les solutions suivantes: $NiCl_2$ 0.01*M*, nioxime 0.0563*M*, NH_4SCN 60%, HCl conc. 36.4%, NH_3 25%, HCl 5*N*, NH_3 5*N*.

Mode opératoire. On dissout 0.2 à 0.7 g du sel de cobalt à doser dans 5 ml de HCl 5*N* directement dans le compartiment A du séparateur Fig. 1. On ajoute 10 ml de la solution NH_4SCN qui fait apparaître la couleur bleue du thiocyanate de cobalt. On introduit 10 ml d'acétate d'éthyle et fait passer le tout dans le compartiment B Fig. 1. Lorsque le solvant a atteint sa couleur maximum on laisse décanter et sépare le solvant comme indiqué à la p. 447. On ajoute 0.1 ml HCl conc. puis une nouvelle quantité de solvant (10 ml). On vérifie au papier indicateur le pH qui doit être inférieur à 2 et on recommence l'opération jusqu'à ce que l'acétate d'éthyle ne présente plus de coloration. La dernière extraction terminée, on reçoit dans une ampoule à décanter la solution aqueuse qui s'écoule par F. On lave A et B du séparateur par 3 ml de NH_3 5*N*, puis 2 ml d'eau distillée. Le pH est porté à une valeur comprise entre 5 et 10

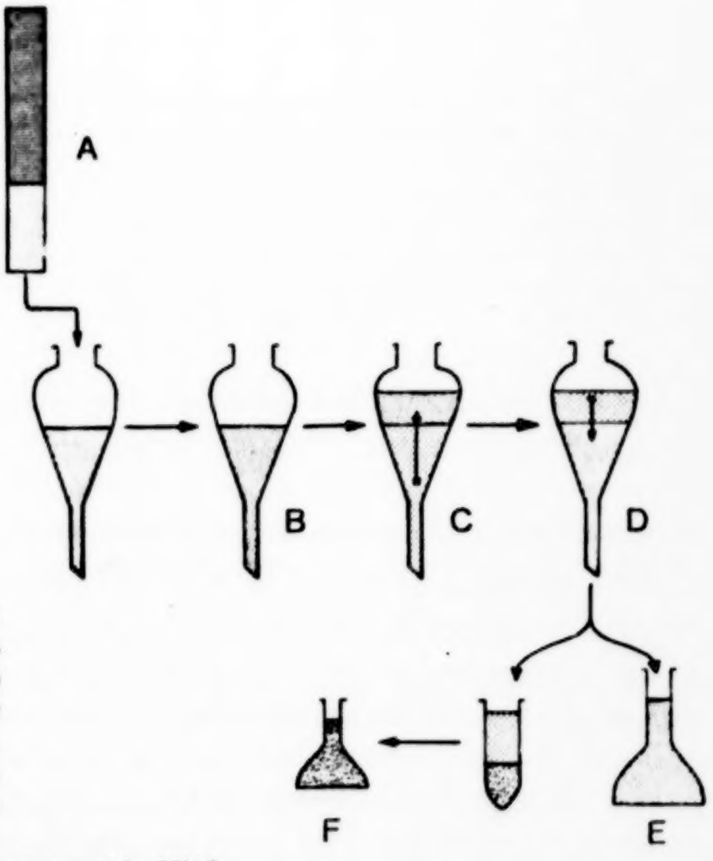

Fig. 5. Schéma de la séparation du cobalt: A: séparateur; B: précipitation du Ni par la nioxime; C: passage de la Ni-nioxime dans le benzène; D: dissociation de la Ni-nioxime et passage du Ni en solution aqueuse; E: dosage du Ni par mise en suspension de la Ni-nioxime; F: dosage du Ni par mise en solution de la Ni-nioxime dans la quinoléine.

▦ Solution aqueuse contenant le Ni^{+2};

▨ Phase contenant les ions autres que le Ni^{+2};

▩ Phase contenant la Ni-nioxime en suspension;

■ Solution organique contenant le cobalt;

■ Quinoléine + Ni-nioxime en solution.

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par addition de NH_3 5*N*, puis on précipite le nickel par 5 ml de nioxime 0.0563*M*. Après 10 minutes, la Ni-nioxime renfermée dans l'ampoule à décanter est séparée des dernières traces de cobalt au moyen du benzène (10 ml). On agite pour provoquer l'émulsion. La Ni-nioxime passe dans la phase organique. On sépare les deux liquides, élimine la solution aqueuse, lave le benzène trois fois avec 5 ml de NH_3 5*N* et deux fois avec 5 ml d'eau bidistillée. La dernière portion de NH_3 doit être incolore. Le nickel passe en solution aqueuse lorsqu'on ajoute 5 ml de la solution HCl 5*N*. Après agitation, on laisse décanter puis on reçoit la solution chlorhydrique dans un ballon jaugé de 50 ml. On lave deux fois le solvant avec 5 ml d'eau pour récupérer les dernières traces de nickel retenues par le benzène et les parois de l'ampoule, puis on dose le nickel par une des deux méthodes citées. Dans le cas présent, celle de FERGUSON ET BANKS est plus rapide que la nôtre, aussi l'avons nous utilisée.

Les dosages ont été effectués sur le chlorure de cobalt et sur le nitrate de cobalt de la maison Merck. Les résultats sont donnés dans le Tableau XII et le schéma du processus d'extraction dans la Fig. 5.

TABLEAU XII

$CoCl_2 \cdot 6\,H_2O$ Merck „Nickelfrei" Lot. No 84.327 Prise 1.0 g					
Ni ajouté μg	*Ni total trouvé* μg	*Ni dans le sel* μg	*Rapport* Ni/Co	*Ni dans le sel* %	*Erreur* %
118	238	120	1/1050	0.0120	±2.5
59	178	119	1/1400	0.0119	±2.0
0	116	116	1/2000	0.0116	±1.5
$Co(NO_3)_2 \cdot 6\,H_2O$ Merck garantie Ni < 0.001% Lot No 321.913 Prise 3.4 g					
0	23	23	1/30.000	0.00068	±2.5
59	84	35	1/8215	0.00073	±3.0
118	142	24	1/4155	0.00070	±2.0

Les erreurs ont été calculées en tenant compte des valeurs extrêmes trouvées pour le nickel total sur une série de 6 dosages.

2. *Séparation et dosage du nickel dans un mélange de plusieurs cations*

Pour mettre à l'épreuve la sélectivité de notre méthode d'extraction, nous avons effectué le dosage du nickel en présence d'importantes quantités de Cu^{+2}, Al^{+3}, Fe^{+3} et Ca^{+2}. La solution renferme 1 mg/ml des sels suivants: $CuCl_2$, $Al(NO_3)_3$, $Fe(NO_3)_3$ et $CaCO_3$. Ils ont été dissous dans l'acide chlorhydrique 5*N*. Comme les substances utilisées pro anal renferment des traces de nickel, nous avons fait le dosage du nickel sur ce mélange, pour obtenir le blanc, puis des quantités variables de nickel ont été ajoutées et le nickel total dosé. Les résultats sont donnés dans le Tableau XIII. Il a été procédé de la façon suivante: Des essais préliminaires ont montré que, même dans ce cas, une préextraction au thiocyanate est à recommander. On élimine ainsi la plus grande partie des ions gênants. La solution est introduite dans le compartiment A (Fig. 1) du séparateur et on procède comme il a été dit à la p. 453, seul change le pH auquel on effectue la séparation au moyen du benzène. En effet, après l'extraction au thiocyanate, on porte la solution au pH 3.5 par addition de NaOH N (papier indicateur), lave les compartiments A et B avec une solution tampon pH 3.5 (acide acétique 0.185N + acétate de sodium 0.015M). Le benzène est lavé une première fois avec 5 ml de la solution tampon puis 2 fois avec 5 ml de NH_3 N et une dernière fois au moyen de 5 ml d'eau distillée. Le nickel est dosé selon la méthode décrite à la p. 448. Les résultats des dosages sont donnés ci-dessous.

TABLEAU XIII

Ni dans 5 ml de solution de base µg	*Ni ajouté µg*	*Ni total µg trouvé*	*Ni ajouté trouvé µg*
13.5	59.0	75	61.5
12.8	88.5	102	89.2
13.2	59.0	72	58.8

CONCLUSIONS

La méthode de séparation préconisée est satisfaisante et présente une bonne sélectivité, elle permet de doser quelques gammas de nickel en présence de grandes quantités de la plupart des cations et avec une bonne précision. Le temps pour effectuer deux dosages est d'une heure environ. On trouvera plus de détails sur ce travail dans la thèse de W. HAERDI[6].

RÉSUMÉ

La méthode de séparation proposée permet de doser le nickel en présence d'une grande quantité d'ions étrangers. Elle consiste à extraire la nickel-nioxime précipitée en solution aqueuse par le benzène. Celle-ci passe quantitativement dans ce dernier sans se dissoudre. Après élimination de l'eau, le benzène est repris par une solution chlorhydrique, dans laquelle la nickel-nioxime se dissout. On peut ainsi séparer le nickel d'un grand nombre de cations. Cependant, s'ils sont en trop grande proportion, il est préférable d'effectuer une préextraction au thiocyanate, dans l'acétate d'éthyle. Il a aussi été établi une méthode de dosage du nickel par la nioxime en dissolvant le complexe dans la quinoléine, ce qui permet de doser de 2 à 35 µg de nickel. Nous avons appliqué cette méthode de séparation à la détermination du nickel dans les sels de cobalt Merck (chlorure et nitrate) et nous avons montré que ce dosage était encore possible pour 1 partie de nickel dans 30.000 de cobalt.

SUMMARY

A method is described for the separation and determination of µg-quantities of nickel in the presence of large quantities of foreign cations, by extracting nickel-nioxime with organic solvents.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Trennung und Bestimmung von µg-Mengen Nickel neben grossen Mengen anderer Kationen durch Extraktion von Nickel-nioxim mit organischen Lösungsmittel.

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SUB-MICROGRAM-SCALE ANALYSIS BY COULOMETRY AT CONTROLLED POTENTIAL

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INTRODUCTION

The utility of coulometry at controlled potential in analyses at the decigram to milligram level is now well established, but the practical problems involved in securing accurate current integrations at that level have been solved too recently to permit any concern with the further problems that may be expected to arise in dealing with much smaller amounts of material. Meanwhile many successful applications of coulometry at controlled current to microgram-scale analyses have been described. These facts have led to a general belief that the controlled-current technique is the more useful of the two in trace analyses.

This belief has been held despite the demonstration by LORD, O'NEILL, AND ROGERS[1] that even millimicrogram amounts of silver can be determined with good accuracy by a procedure which, though quite different in apparatus and methodology, conforms to any operational definition of coulometry at controlled potential. More recently, using more conventional procedures, BOOMAN, HOLBROOK, AND REIN[2] have succeeded in determining 7.5 μg of uranium with a standard deviation of ± 2.2%, while MEITES[3] was able to obtain a mean deviation of ± 1.0% in the determination of 5.2 μg of chromium.

The present paper describes the results of an attempt to extend coulometry at controlled potential to its extreme lower limit, using a chemical system which was believed to be ideally suited to that purpose together with conventional apparatus and techniques for current integration. This attempt was made, partly in pursuance of the considerations described above, and partly in the hope of casting new light on the sources of error which afflict all analyses by coulometry at controlled potential and on the techniques by which these errors can be eliminated.

EXPERIMENTAL

The Analytical Instruments, Inc. (Bristol, Conn.) potentiostat and electromechanical current integrator employed have been described elsewhere[4]. All electrolyses were carried out in a double-diaphragm cell[4], using a well-stirred mercury pool working electrode having an area of 47 cm^2, a commercial fiber-type saturated calomel reference electrode, and a helical platinum wire auxiliary electrode. A few drops of saturated hydrazine dihydrochloride were added to the supporting electrolyte solution in the auxiliary electrode compartment of the cell to prevent anodic attack of the platinum. A 1.5-V dry cell in series with the auxiliary electrode was used to permit the potentiostat to maintain control throughout each electrolysis in which the working electrode was anodic[3]. Where necessary, a decade resistance box in series with the bias battery was employed to limit the initial current to a value just smaller than the rated maximum value for the integrator input resistor employed. This unusual step was prompted by the extremely rapid decrease of the electrolysis current: had an input resistor been used which was small enough to bring about accurate integration of the initial current, too few counts would often have been secured to permit the maximum precision to be attained. Measurements of the electrolysis current were made with a multi-range milliammeter in the electrolysis circuit.

Oxygen was excluded from the working electrode compartment of the cell by a very rapid stream of prepurified nitrogen which had been passed through two efficient gas-washing bottles containing 0.1 *F* chromous chloride, 1 *F* hydrochloric acid, and excess heavily amalgamated zinc, then through a similar bottle containing water, and finally through still another bottle containing the ammoniacal supporting electrolyte used. The first and second of these bottles served to remove the trace of oxygen present in the nitrogen[3], the third to trap droplets of chromous chloride that might have been sprayed over, and the fourth to prevent excessive volatilization of ammonia from the solution being electrolyzed.

A stock 0.05*M* solution of zinc ion in 0.2*F* hydrochloric acid was prepared determinately from pure metallic zinc. More dilute zinc solutions were prepared from this by dilution with 0.2 *F* hydrochloric acid, using carefully calibrated volumetric glassware. Other chemicals used were ordinary reagent grade.

"Vacumetal" mercury (Metalsalts Corp., Hawthorne, N. J.) was used without further purification in all determination involving as much as 0.5 mg of zinc, but the ammonia and ammonium monohydrogen citrate used to prepare the supporting electrolyte contained enough zinc to cause a detectable error even at the 5-mg level. Hence the supporting electrolyte was usually freed from zinc immediately before use by an electrolysis at −1.50 V *vs.* S.C.E.; the zinc amalgam formed in this step was drained out of the cell and replaced by fresh mercury before the actual analysis was commenced. For determinations of less than 0.5 mg of zinc, mercury was used which had been previously purified by anodic stripping into purified ammoniacal citrate at −0.50 V *vs.* S.C.E.

DATA AND DISCUSSION

The sensitivity of coulometry at controlled potential is ultimately limited by the magnitude of the correction that must be made for the background quantity of electricity, *i.e.*, the quantity of electricity which is consumed at the working electrode by processes other than the one of interest. Five components of this background quantity of electricity have been distinguished by MEITES AND MOROS[5], but only three are relevant to the determination of zinc by the present method. These are the "charging" or "condenser" quantity of electricity, Q_c, required to charge the working electrode and the electrical double layer at its surface up to the control potential; the "faradaic impurity" quantity of electricity, $Q_{f,i}$, required to oxidize or reduce impurities in the mercury and the supporting electrolyte; and the "continuous faradaic" quantity of electricity, $Q_{f,c}$, which results from the reduction of hydrogen ion, water, ammonium ion, or some other constituent of the supporting electrolyte whose concentration remains substantially unchanged throughout the electrolysis.

When the working electrode area is about 50 cm², as was the case in this investigation, Q_c could hardly exceed 10 mμ F$_y$, as pointed out by MEITES AND MOROS. It is therefore significant only at or below the microgram level. The value of $Q_{f,i}$ has no such natural limit, but it can be made negligibly small by appropriate preliminary purification of the mercury and the supporting electrolyte. When this is done, Q_c can be measured directly by the procedure illustrated by Fig. 1(a). To minimize difficulties that might otherwise be caused by traces of surface-active materials which affect the capacity of the double layer, it is preferable to determine Q_c immediately before the addition of the sample, using the same mercury and supporting electrolyte that will be used in the later analysis. The values of Q_c thus obtained differ appreciably from one run to the next, but the fact that an absolute error of ± 0.2 mμ-equiv. could be achieved in the determination of zinc indicates that each individual value of Q_c is probably meaningful to within a few %.

Whereas Q_c is essentially completely accumulated within a second or two after the start of the electrolysis*[,5,6] and $Q_{f,i}$ approaches a constant value in accordance with LINGANE's equation[7], $Q_{f,c}$ increases linearly with time and thus represents an error which increases virtually indefinitely as the electrolysis is prolonged. This error can, it is true, be eliminated by making periodic measurements of $\acute{Q}_{total}$, the total quantity of electricity accumulated, at times so long that the desired working electrode reaction is complete, and extrapolating $\acute{Q}_{total}$ to zero time. An example of this procedure was given by MEITES AND MOROS[5]. In practice, however, the uncertainty introduced by this extrapolation becomes intolerably large on the submicrogram scale unless the continuous faradaic current is very small or the extrapolation very short.

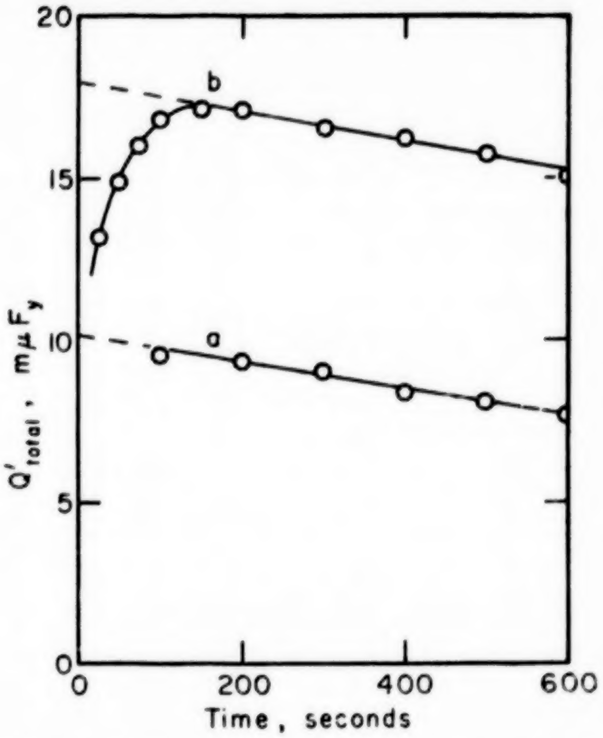

Fig. 1. Variation of Q'_{total} with electrolysis time during typical electrolyses of (a) 65 ml of electrolytically purified 2 *F* ammonia–1 *F* ammonium citrate with 25 ml of electrolytically purified Hg, and (b) same + 0.007802 μequiv. (0.255 γ) of zinc. The data were secured at −0.50 V *vs.* S.C.E. immediately after an electrolysis at −1.40 V *vs.* S.C.E.

From these considerations it is obvious that the best sensitivity and accuracy will be secured when the final current integration is performed during an electrolysis which proceeds very rapidly and which involves only a very small continuous faradaic current.

The first of these desiderata is rather difficult to achieve when the substance being determined is initially in the solution phase. This is because the rate of the electrolysis then depends, according to LINGANE's equation[7], on the diffusion coefficient of the ion or molecule being reduced, on the ratio of electrode area to solution volume, and on the thickness of the Nernst diffusion layer. By using a large efficiently stirred working electrode and the minimum possible volume of solution, it is generally possible to achieve 99.9% completion in about 15 min. But a further substantial increase in this rate can be effected only by increasing the diffusion coefficient of the species being determined.

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* This is not true when the initial current is limited by the insertion of a series resistor into the electrolysis circuit, as was sometimes done in this work, because the working electrode potential then drifts with time up to the control potential, so that the accumulation of Q_c becomes complete only when the electrolysis current begins to fall below the artificially imposed limit. This, however, has no effect on the final value of Q_c.

This could be done by raising the temperature, but this approach is neither practical nor useful. Taking the ordinary temperature coefficient of the diffusion coefficient as +2% per degree, increasing the temperature from 25° to 95° during an electrolysis would barely quadruple the electrolysis rate. To be sure, this might be a profitable approach for the routine analytical laboratory which is desirous of obtaining the greatest possible use from its instrument. On the other hand, it is useless in submicrogram analysis, because $i_{f,c}$ increases with increasing temperature, and in the extrapolation to zero time this introduces an increased uncertainty which more than counterbalances the advantage derived from increasing the rate of the electrolysis.

In the present work, advantage was taken of the fact that the diffusion coefficient of a metal dissolved in mercury is often considerably larger than that of a metal ion in aqueous solution[8]. Thus, from LINGANE's data on the polarographic diffusion current constant of zinc(II) in ammoniacal ammonium chloride[9], the diffusion coefficient of this ion at 25° is calculated from the Ilkovic equation to be $9.9 \cdot 10^{-6}$ cm^2/sec. The diffusion coefficient of zinc in mercury has been measured by MEYER[10], VON WOGAU[11], WEISCHEDEL[12], and FURMAN AND COOPER[13]; from the concordant results of WEISCHEDEL and FURMAN AND COOPER, one estimates that in very dilute amalgams the diffusion coefficient of zinc is approximately $1.7 \cdot 10^{-5}$ cm^2/sec. Therefore the anodic stripping of zinc should proceed almost twice as rapidly as the cathodic deposition of zinc ion if the volumes of solution and mercury are identical and if the Nernst diffusion layer thicknesses are the same for the anodic and cathodic processes. In fact, however, it is easy to carry out an electrolysis with only one-half to one-fourth as much mercury as solution, and in addition it appears that the Nernst diffusion layer thickness for the anodic process is appreciably smaller than for the cathodic process. The actual rates of these two processes in a typical experiment are indicated by Fig. 2, which shows that the stripping is 99.9% complete within about 3 min.

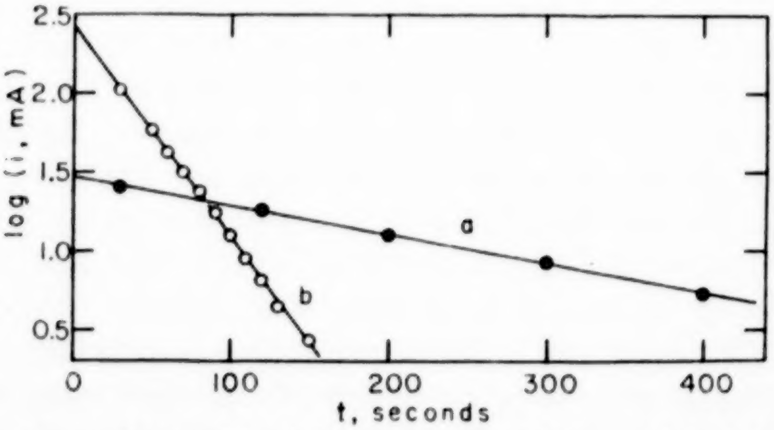

Fig. 2. Current–time curves obtained for (a) the reduction of 80 μequiv. of zinc from 50 ml of 2 *F* ammonia–1 *F* ammonium citrate at −1.45 V *vs.* S.C.E., and for (b) the subsequent reoxidation of the same quantity of zinc from the 25-ml amalgam electrode at −0.70 V *vs.* S.C.E.

The extreme rapidity of the stripping process permits the correction for $i_{f,c}$ to be made by means of a very short extrapolation, and in addition it is a simple matter to carry out the stripping at a potential where $i_{f,c}$ is very small. As was pointed out above, these conditions are essential to the success of controlled-potential coulometric analyses on the submicrogram level.

An ammoniacal ammonium citrate supporting electrolyte was selected for this work on the basis of polarographic data secured by KARP AND MEITES[14,15], which indicated that such a medium should be well suited to the determination of zinc in the presence of other elements commonly encountered in non-ferrous alloys. A "2 *F* ammonia–1 *F* ammonium citrate" solution (3 moles of ammonia and one mole of diammonium hydrogen citrate per liter) was used to minimize the cell resistance and to enable substantial concentrations of metal ions to be handled. Fig. 3 shows typical current–potential curves of zinc(II) and zinc amalgam in this medium. From these curves it is apparent that zinc(II) can be quantitatively reduced at any potential more negative than about —1.35 V *vs.* S.C.E., and that zinc can be quantitatively stripped out of the amalgam at any potential more positive than about —1.20 V *vs.* S.C.E. To avoid any formation of ammonium amalgam, which would lead to a high and erratic consumption of electricity in the stripping step, it is preferable to carry out the deposition at —1.40 or —1.45 V *vs.* S.C.E. In dealing with substantial amounts (0.1 mg or more) of zinc, good results can be secured by carrying out the stripping at —1.00 V even if the continuous faradaic current is neglected. However, the correction for $i_{f,c}$ at such negative potentials becomes undesirably large when smaller quantities of zinc are involved, and hence for maximum sensitivity it is preferable to carry out the reoxidation at about —0.50 V.

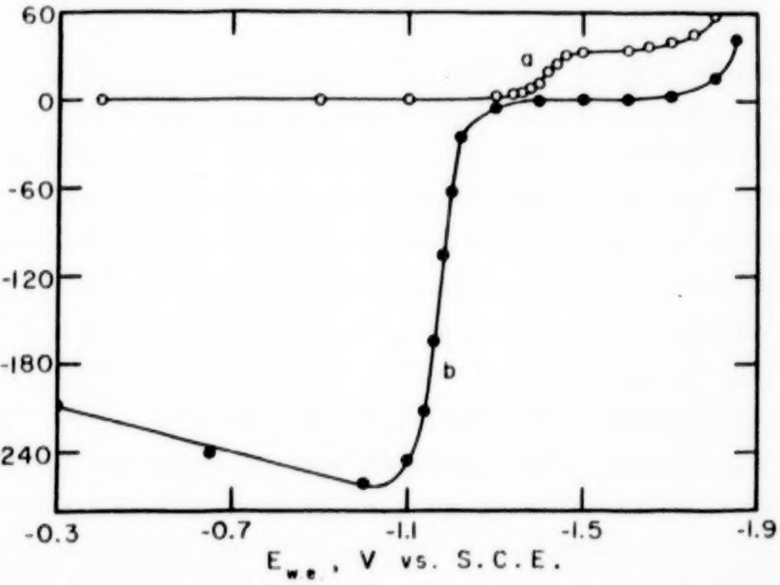

Fig. 3. Current–potential curves for (a) 0.6 m*M* zinc (II) in 2 *F* ammonia–1 *F* ammonium citrate, and (b) the amalgam electrode prepared by the quantitative reduction of 50 ml of the solution of curve *a* with 25 ml of mercury at —1.45 V *vs.* S.C.E.

Attention may be called to the fact that the amalgam electrode at the completion of the deposition step is at a potential where $i_{f,c}$ is by no means negligible. If the amalgam is then allowed to stand with the electrolysis current off, the zinc will reenter the solution at a rate which is proportional to this value of $i_{f,c}$. Especially when dealing with small amounts of zinc, therefore, it is essential to begin the stripping as rapidly as possible after the reduction is completed.

TABLE I

COULOMETRIC DETERMINATION OF ZINC

Microequivalents Zn taken		*Number of determinations*	*Average microfaradays consumed*		*Error of mean, %*
1986.8	(65 mg)	4	1988.6	± 0.11%	+ 0.09
991.2		3	991.6	± 0.11%	+ 0.04
398.1		4	397.7	± 0.07%	— 0.10
159.85		2	159.8_7	± 0.03%	+ 0.01
59.28		2	59.27	± 0.02%	— 0.02
19.75_2		3	19.73_4	± 0.07%	— 0.09
7.857		2	7.858	± 0.00%	+ 0.01
2.368_9		3	2.370_0	± 0.04%	+ 0.05
0.7857		2	0.7852	± 0.05%	— 0.06
0.2352		5	0.2356	± 0.14%	+ 0.17
0.07791		3	0.07724	± 0.34%	— 0.8
0.02346		6	0.02359	± 0.5 %	+ 0.4
0.007802		4	0.00767	± 2.8 %	— 1.7
0.002298	(0.07 µg)	8	0.00219	± 10.3 %	— 5

Table I shows the results obtained when the method just described was applied to solutions containing known amounts of zinc. With quantities of zinc exceeding about 10 µg, an accuracy and precision of ± 0.1% are easily attainable. Even 1 µg of zinc can be determined with an accuracy and precision of ± 1% or better; this is comparable with what has been achieved by coulometric titrations under equally favorable conditions. As little as 0.07 µg of zinc can be determined with an accuracy and precision of about ± 10%, which corresponds to an uncertainty of about 0.2 mµ Fy.

This last value represents about 2% of the value of Q_c under these conditions. It is therefore apparent that the ultimate sensitivity of controlled-potential coulometric analysis is governed primarily by the accuracy with which the necessary correction for Q_c can be determined. A significant improvement in the relative error involved in this determination appears somewhat improbable, and hence it seems safe to say that the further extension of controlled-potential analysis into the millimicrogram range will be possible only if Q_c can be reduced well below its value under these conditions. In principle this can be achieved in three ways. One is by considerably decreasing the area of the working electrode, which will cause a proportional decrease in the value of Q_c; this must be accompanied by a roughly proportional change of solution volume if electrolyses* are not to be unduly prolonged. This involves some difficulties, though by no means insuperable ones, in cell design. Another is to decrease the extent to which the working electrode potential is altered during the electrolysis: here this was 0.9 V, and this corresponds much more nearly to a maximum than to a minimum change. This, however, is not a truly general solution, for the potential change during any particular procedure is governed partly by the electrochemistry of the substance being determined and partly by the necessity of minimizing $i_{f,c}$ during the final electrolysis, and these are matters outside of the experimenter's control. A final possibility would involve adding to the solution a capillary-active substance whose adsorption at the electrode surface would lead to a considerable decrease of the double layer capacity.

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* Including, for example, the deposition step in the present procedure.

SUMMARY

The considerations which determine the success of controlled-potential coulometric analyses on the submicrogram level are discussed, and it is shown that the ultimate sensitivity of the method is governed by the accuracy with which the requisite background corrections, especially that for the charging quantity of electricity, can be determined. A method for the coulometric determination of zinc based on these considerations is shown to contain a limiting uncertainty of ± 0.2 mμF$_y$, so that as little as 0.07 μg of zinc can be determined within about ± 10%, while quantities of zinc exceeding about 10 μg can be determined with an accuracy and precision of ± 0.1% or better. Possible techniques for the further extension of controlled-potential coulometric analysis into the millimicrogram range are briefly discussed.

RÉSUMÉ

On examine les conditions d'application, à l'échelle ultramicrochimique, des analyses coulométriques à potentiel contrôlé. L'essai d'un dosage coulométrique de zinc montre qu'il est possible de déterminer jusqu'à 0.07 μg de cet élément avec environ ± 10% d'erreur, tandis que des quantités de zinc dépassant 10 μg peuvent être dosées avec une précision de ± 0.1% (ou même meilleure).

ZUSAMMENFASSUNG

Es werden die Faktoren untersucht, welche die Ergebnisse coulometrischer Analysen mit kontrolliertem Potential bei Submikrogramm-mengen beeinflussen. Die coulometrische Bestimmung von Zink, unter Berücksichtigung dieser Faktoren, erlaubt Mengen bis zu 0.07 μg mit ca ± 10% Genauigkeit und Mengen von mehr als 10 μg mit ± 0.1% Abweichung zu erfassen.

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COULOMETRIC TITRATION WITH ELECTROGENERATED +2 TIN

DETERMINATION OF IODINE, BROMINE, AND VARIOUS OXIDANTS VIA IODOMETRY

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Although the roster of coulometric titrations now includes many reactions of classical titrimetry[1], the use of electrogenerated +2 tin as a coulometric titrant has not previously been reported. We have found that in an acidic bromide medium +4 tin (probably $SnBr_6^{-2}$) is reduced to the +2 state (probably $SnBr_4^{-2}$) with 100% current efficiency at a gold cathode. The formal potential of the stannic–stannous couple in bromide medium is +0.27 V *vs.* N.H.E., a value sufficiently reducing so that (in principle) +2 tin should serve for the titration of divers oxidants.

In practice one encounters the inconvenience that the rate of reduction of most substances by +2 tin is relatively small, but this can be circumvented by either of two means. Firstly, an excess of +2 tin can be generated in the test solution, and, after a short waiting period, the polarity of the generating electrode is reversed from cathode to anode and the excess +2 tin is titrated by the bromine electrogenerated at the anode. The other expedient, applicable to the determination of substances capable of oxidizing iodide to iodine, is "coulometric iodometry". An excess of iodide ion is added to the test solution, and the liberated iodine is titrated with the electrogenerated +2 tin. The iodine–stannous reaction is rapid, and equivalence points can be detected accurately either potentiometrically or amperometrically.

ROWLEY AND SWIFT[2] determined iodine (and thus various oxidants *via* iodometry) by adding a measured excess of standard thiosulfate solution, and back titration of the excess thiosulfate with electrogenerated iodine. This method suffers from the disadvantage of requiring a standard thiosulfate solution, and is only semi-coulometric. Derect titration of iodine with electrogenerated +2 tin is simpler and more convenient.

EXPERIMENTAL

The coulometric titrations were performed in the usual manner[1]. The titration cell, whose capacity was *ca.* 175 ml, is shown in Fig. 1. The auxiliary electrode is separated from the titration chamber by two sintered glass disks, so that interchamber transfer is effectively minimized. The test solution was stirred efficiently with a magnetic stirrer.

Because oxygen is reduced concomitantly with +4 tin at the cathode, elimination of dissolved air from the solution is necessary. By using a non-oxygen producing auxiliary electrode (*e.g.* a cadmium rod in 0.5*M* cadmium chloride), and passing nitrogen through all of the chambers, oxygen was effectively excluded.

In most titrations of iodine, a gold generator cathode (1 × 1 cm) was employed. A platinum generator cathode (1 × 1 cm) was used in titrations of bromine, since bromine oxidizes gold in a bromide medium. Both bromine and iodine were generated at platinum anodes (1 × 1 cm).

The supporting electrolyte was $4M$ sodium bromide, $0.2M$ stannic chloride and $0.2N$ hydrochloric acid. The solution was first deaerated, and then made $0.01M$ in respect to potassium iodide when iodometric determinations were to be performed. The sample of the oxidant to be titrated was then added. Nitrogen was passed only over the surface of the solution during the titration to avoid volatilization of the bromine or iodine.

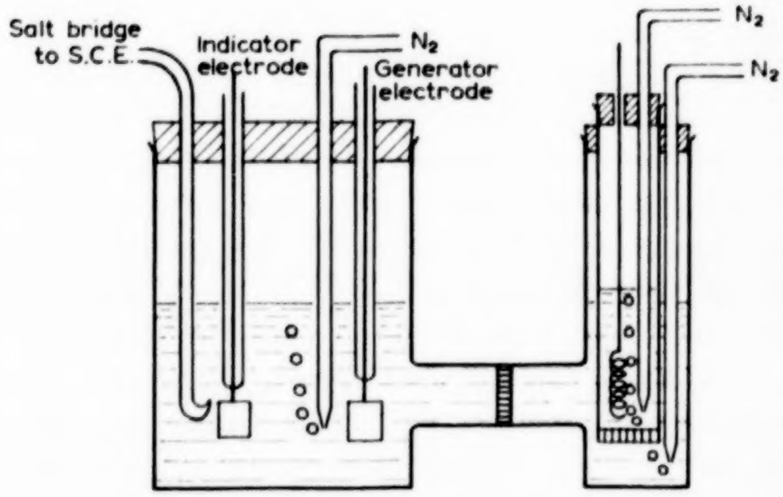

Fig. 1. Coulometric titration cell.

Potentiometric end-point detection with a platinum foil indicator electrode and saturated calomel reference electrode followed the usual practice. The amperometric detection system comprised two identical platinum electrodes (1 × 1 cm) across which 150 mV applied voltage was maintained. The indicator current was observed with a shunted galvanometer. Detailed discussions of both these end-point detection techniques as applied to coulometric titration are available in *Electroanalytical Chemistry*[1].

Current-efficiency for electrogeneration of +2 tin

The electrogeneration of +2 tin was studied only in bromide and chloride media, because it is known from polarographic data that +4 tin produces well delineated reduction waves only in these media. Current efficiencies for the reduction of stannic ion in various chloride and bromide media at gold and platinum cathodes were estimated from current–potential curves with and without stannic ion present[1]. The same cell and conditions used for the coulometric titrations were employed.

These current–potential curves predicted current efficiencies closer to 100% with a gold cathode than with platinum, because gold has a higher hydrogen overvoltage. Although 100% current efficiency is not easily attainable in a chloride medium, a bromide medium (*ca.* $3M$) proved successful. The current efficiency is higher in bromide than in chloride medium because the bromostannate ion requires less overpotential for its reduction, and thus is reduced to the stannous state more in advance of hydrogen ion reduction, than the chloro-stannate ion.

A relatively large bromide ion concentration is necessary to maintain the major part of the +4 tin as $SnBr_6^{-2}$, and hydrogen ion also is essential to prevent its hydrolysis. With 0.2*M* stannic tin the bromide ion concentration must be at least 2.8*M*, and 3 to 4*M* is optimum. A range of hydrogen ion concentration from 0.15 to 0.4*M* is satisfactory. At lower acidities hydrolysis of $SnBr_6^{-2}$ occurs, while at higher acidities hydrogen ion reduction concomitantly with reduction of $SnBr_6^{-2}$ becoms significant.

The supporting electrolyte finally selected as optimum was 4*M* sodium bromide, 0.2*M* stannic chloride, and 0.2*N* hydrochloric acid. Bromide complexes stannic tin more strongly than chloride does, so the electrochemistry of this solution is characteristic of $SnBr_6^{-2}$.

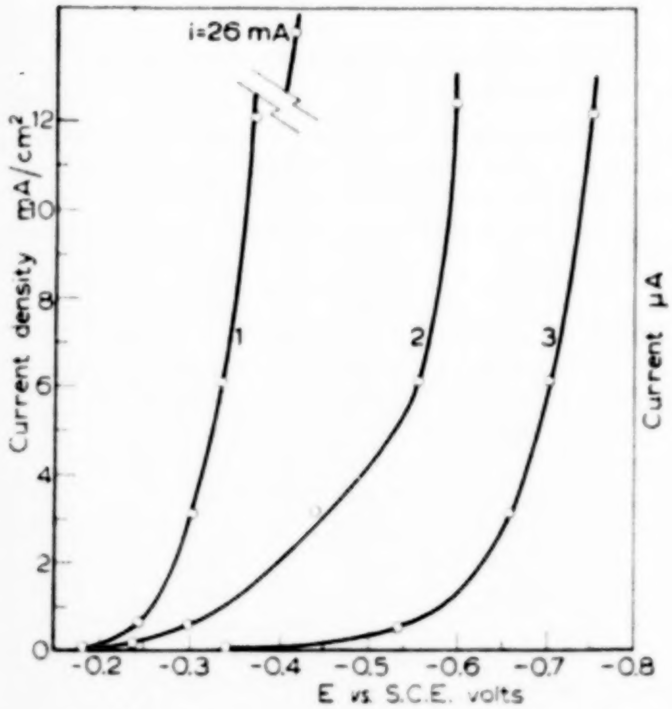

Fig. 2. Increase of hydrogen overpotential by tin oxide film on platinum cathode. In all cases the supporting electrolyte was air-free 3*M* sodium bromide and 0.4*M* perchloric acid, the area of the platinum cathode was 1.68 cm², and the solutions were stirred. (2) Supporting electrolyte alone with clean (unfilmed) platinum cathode. (3) Supporting electrolyte alone but cathode carried a film of hydrous stannic oxide. (1) 0.2*M* stannic chloride present.

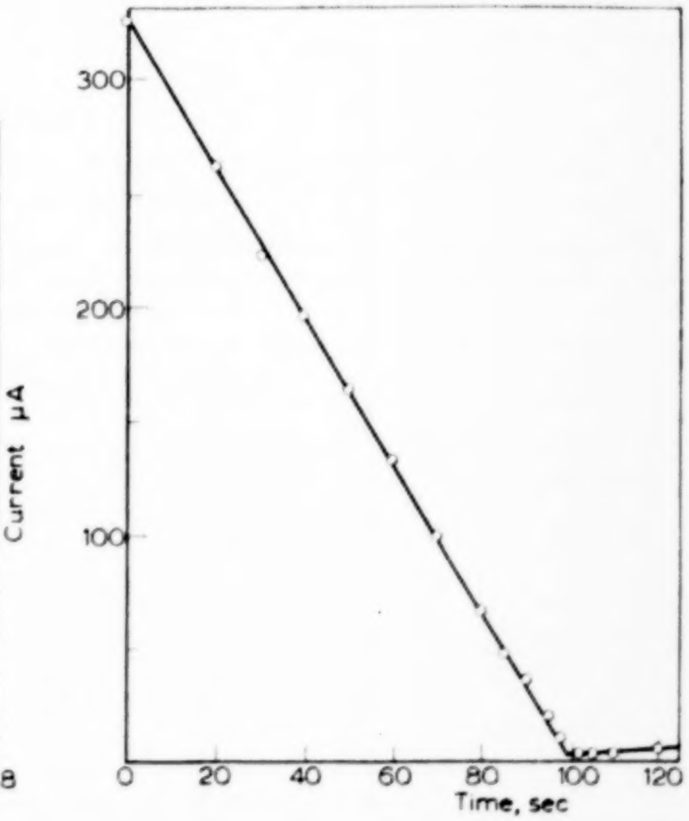

Fig. 3. Typical amperometric titration curve of 2.70 mg of iodine with electrogenerated +2 tin, using two 1 cm² platinum indicator electrodes subjected to an applied voltage of 150 mV.

With a *freshly cleaned* platinum cathode the current efficiency for reduction of $SnBr_6^{-2}$ is considerably short of 100%. However, once the platinum cathode has been used it functions nearly as efficiently as gold. During the reduction of the +4 tin the platinum cathode acquires a film of stannic hydrous oxide, which increases the hydrogen overpotential by about 150 mV and thus greatly minimizes co-reduction of hydrogen ion. This beneficial phenomenon is demonstrated by the current–potential curves in Fig. 2, and it will be discussed in detail in a separate communication. The film of stannic hydrous oxide is not removed by even prolonged washing with water, nor by gentle wiping with filter paper, so that no special care is needed in handling the filmed electrode. The film can be removed with hot hydrochloric or hydrobromic acids or sodium hydroxide.

The current efficiencies predicted from the current–potential curves were verified by direcly determining the amount of +2 tin produced under a particular set of conditions as follows. The +4 tin solution was electrolyzed at either a platinum or gold cathode with a known current for a measured time. The +2 tin produced was then back-titrated with electrogenerated iodine, employing an amperometric end-point as described in a following section. The average current efficiencies at current densities of 10 to 84 mA/cm² was for platinum 99.3 ± 0.2%, and for gold 99.7 ± 0.2%. With both electrodes the current efficiency decreased at current densities below 5 mA/cm².

TABLE I

COULOMETRIC TITRATION OF IODATE, IRON, AND CERIUM (IODOMETRICALLY) WITH ELECTROGENERATED STANNOUS ION

The solution was 4*M* sodium bromide, 0.2*N* hydrochloric acid, 0.008*M* potassium iodide, and 0.2*M* stannic chloride, with a volume of *ca.* 50 ml. A gold generator cathode (1 × 1 cm) was used, except as noted

Substance titrated	*No. of trials*	*Current (mA)*	*Taken (mg)*	*Found (mg)*	*Mean deviation (mg)*	*Av. error %*	*End-point*
Iodate	3	10.10	0.7174	0.7173	0.0007	—0.05	Amp.
	3	22.78	1.794	1.795	0.001	+0.02	,,
	3	22.90	1.891	1.894	0.005	+0.2	,,
	3	22.89	1.891	1.892[a]	0.005	+0.1	,,
	3	33.11	3.587	3.592	0.007	+0.1	,,
	1	22.98	1.891	1.897[b]	—	+0.3	,,
	1	22.86	1.891	1.889[c]	—	—0.1	,,
	5	10.10	0.3587	0.3595	0.0050	+0.2	Pot.
	3	10.00	0.7174	0.7180	0.0021	+0.05	,,
	3	33.10	3.587	3.578	0.007	—0.3	,,
Iron (+3)	3	10.12	0.5640	0.5635	0.005	—0.10	Amp.
	3	22.78	2.820	2.804	0.012	—0.56	,,
	3	33.14	5.640	5.635	0.011	—0.10	,,
Cerium (+4)	5	23.04	6.663	6.655	0.046	—0.13	,,
	2	33.26	13.33	13.38	0.01	+0.35	,,

[a] Platinum electrode 0.7 × 1.8 cm used.
[b] Solution made 0.06*M* in fluoride.
[c] Solution made 0.10*M* in fluoride.

Titration performance data

Coulometric iodometry. Typical results of the iodometric determination of potassium iodate, +3 iron, and +4 cerium in Table I demonstrate that the titration is precise and accurate.

The shape of the amperometric titration curve is shown in Fig. 3. The current remains small after the end-point because the stannic–stannous couple behaves quite irreversibly, and the applied voltage of 150 mV is smaller than the total cathodic and anodic overpotentials.

Using potentiometric end-point detection, the equivalence point potential is +0.28 V *vs.* S.C.E. The supporting electrolyte was pre-titrated to this potential before the sample was added.

TABLE II

COULOMETRIC TITRATION OF BROMINE WITH +2 TIN

Bromine was produced *in situ* by addition of potassium bromate solution to *ca.* 50 ml of 4*M* sodium bromide, 0.2*M* stannic chloride, and 0.2*N* hydrochloric acid. The generator electrode was platinum, 0.8 × 2.0 cm.

Current (mA)	*Potassium bromate (mg)*		*% Error*
	Taken	*Found*	
23.00	1.265	1.256	—0.7
		1.256	—0.7
		1.262	—0.2
		1.273	0.6
		1.280	1.2
		1.285	1.6
		1.265	0.0
		1.272	0.6
		1.268	0.2
		Av. 1.269 ± 8	0.3
22.82	1.274	1.271	—0.2
		1.281	0.6
		1.280	0.5
		Av. 1.277 ± 4	0.2
33.25	2.530	2.524	—0.2
33.15	2.547	2.544	—0.1
		2.552	0.2
		2.551	0.2
		Av. 2.549 ± 3	0.1
62.06	5.094	5.098	0.1

Direct titration of bromine. Typical results of the titration of bromine (generated *in situ* by the addition of potassium bromate) in Table II demonstrate that bromine may be determined with an average error of 0.2 to 0.3%. The amperometric end-point was similar to that obtained in the iodine titration.

The reaction tends to be slow near the end-point, but a titration can be completed in 5 min. When titrations were performed by successive additions of bromate samples to the supporting electrolyte, the first sample gave results about 0.001 milliequivalent low. Results with subsequent samples were close to the theoretical value. This negative error in the first titration was probably due to reducing impurities in the solution, and was eliminated by generating bromine at a platinum anode, stirring for 5 minutes, and titrating to the end-point with +2 tin, before the sample was added.

Titrations using potentiometric end-point detection were somewhat slower, since the bromine–bromide couple establishes potentials sluggishly at platinum electrodes.

Direct and reverse titrations with the stannous–bromine and stannous–iodine systems

Because a bromide medium is used in generating +2 tin, the stannous–bromine couple (or by addition of a small amount of iodide, the stannous–iodine couple) can be employed *via* back titration in cases where direct titration is not feasible because of a too small reaction rate. By appropriate selection of polarity of the generator electrode in the test solution, bromine can be generated *via* anodic oxidation of bromide ion, or stannous tin can be generated by cathodic reduction of stannic ion. By generation of an excess of +2 tin and back-titration with either bromine or iodine, titration of dyes and other substances which are reduced only slowly by +2 tin is possible. Similarly +2 tin can be used as a back-titrant for slow oxidations, brominations or iodinations.

Typical results in Tables III and IV demonstrate that anodic and cathodic generation times coincide within a few parts per thousand at current densities of 5 to 84

TABLE III

DIRECT AND BACK TITRATIONS WITH THE STANNOUS–IODINE SYSTEM

The solution was 3.5*M* in sodium bromide, 0.2*M* in stannic chloride, 0.2*N* in hydrochloric acid, and 8 m*M* in potassium iodide. The volume was *ca.* 56 ml. The generator cathode was a gold electrode (1 × 1 cm), and the generator anode was of platinum (1 × 1 cm).

Current (mA)	*Substance generated first*	*Iodine gener. time (sec)*	*Stannous gener. time (sec)*
	Amperometric end-point		
5.218	iodine	100.0	100.3
	stannous	99.1	100.0
9.975	iodine	100.0	100.3
	stannous	99.8	100.0
23.06	iodine	100.0	100.0
	stannous	99.4	100.1
41.08	iodine	100.0	100.1
	stannous	99.5	100.0
84.05	iodine	49.98	50.13
	stannous	49.86	49.93
	Potentiometric end-point		
10.05	iodine	100.0	100.1
	stannous	99.7	100.0
20.54	iodine	100.0	100.0
31.34	iodine	100.0	99.9
	stannous	100.0	100.0
86.01	iodine	50.01	50.13
	stannous	49.92	50.00

TABLE IV

DIRECT AND BACK TITRATIONS WITH THE STANNOUS–BROMINE SYSTEM

The solution was $3.5M$ sodium bromide, $0.2M$ stannic chloride, and $0.2N$ hydrochloric acid. The volume was *ca.* 57 ml. The generator electrode was platinum (1 × 1 cm).

Current (mA)	*Substance generated first*	*Bromine gener. time (sec)*	*Stannous gener. time (sec)*
	Amperometric end-point		
9.210	bromine	100.0	100.5
	stannous	99.6	100.0
30.88	bromine	100.0	99.8
	stannous	99.5	100.0
43.80	bromine	100.0	99.8
	stannous	99.6	100.0
73.79	bromine	50.00	49.97
	stannous	49.95	49.99
	Potentiometric end-point		
9.982	bromine	100.0	100.9
	stannous	99.6	100.0
19.81	bromine	100.0	99.9
	stannous	99.8	100.0
31.16	bromine	100.0	99.6
	stannous	99.6	100.0
42.77	bromine	100.0	99.6
	stannous	99.8	100.0
81.66	bromine	50.01	49.89
	stannous	49.87	49.96

mA/cm^2. Amperometric and potentiometric end-point detection both were employed. The equivalence point potential of the bromine–stannous titration is +0.38 V *vs.* S.C.E.

Quinone (*p*-benzoquinone) was chosen as a model organic compound to be titrated with the stannous–bromine system. The curve obtained with a two-electrode amperometric indicating system is shown in Fig. 4 and is typical of the titration of a reversible couple with an irreversible one. The initial current is small, because oxidation of bromide at the indicator anode and reduction of quinone at the indicator cathode take place at potentials farther apart than the impressed voltage (150 mV). As the titration proceeds, the reaction at the indicator anode becomes the oxidation of hydroquinone, and since the quinone–hydroquinone couple is reversible, the indicator current increases. The current reaches a maximum about mid-way through the titration (with indicator electrodes of equal size) and then decreases as more quinone is reduced, the cathode becoming the indicator electrode. Since the stannic–stannous couple is irreversible, the current remains small after the equivalence point.

The fact that the stannous–quinone reaction is somewhat slow renders the direct titration of quinone inconvenient, and a back-titration procedure is preferable. Excess +2 tin was generated, and then the excess was determined by back-titration with bromine.

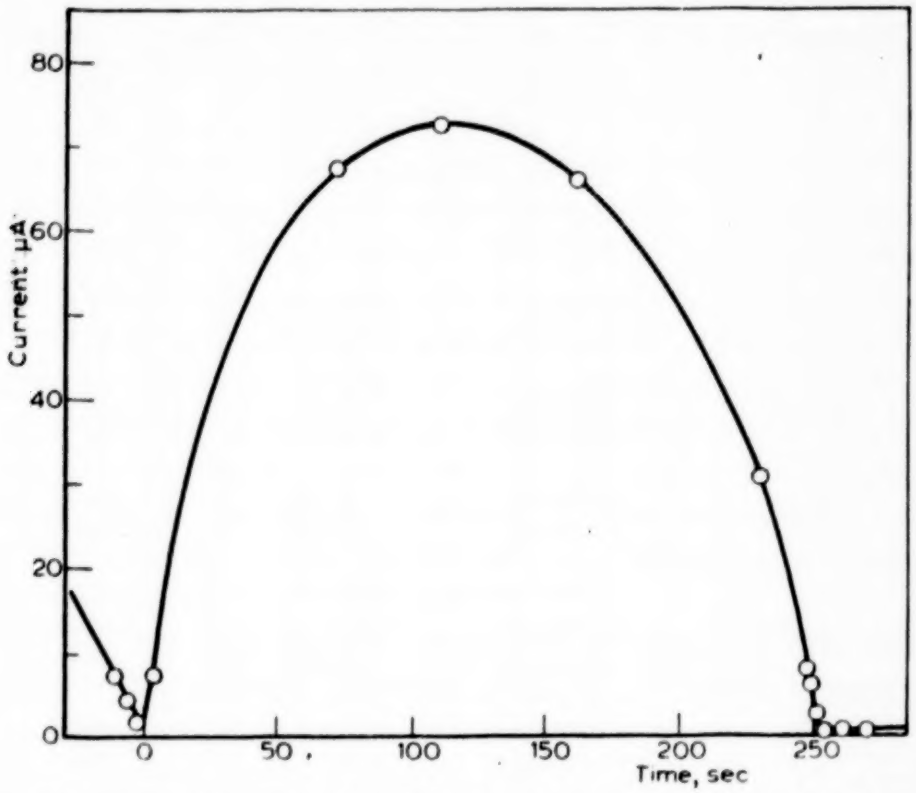

Fig. 4. Amperometric monitoring of coulometric titration of quinone with +2 tin (to the right) and of hydroquinone with bromine (to the left). 3.07 mg of quinone in *ca.* 50 ml of $3M$ sodium bromide, $0.2N$ hydrochloric acid, and $0.2M$ stannic chloride, with 22.8 mA generating current. The two platinum indicator electrodes were subjected to an applied voltage of 150 mV.

TABLE V

COULOMETRIC TITRATION OF QUINONE AND HYDROQUINONE WITH THE STANNOUS–BROMINE SYSTEM

The solution was $3M$ sodium bromide, $0.2M$ stannic chloride, and $0.2N$ hydrochloric acid with a volume of *ca.* 50 ml

Sample	*Current (mA)*	*Quinone (or hydroquinone) taken (mg)*	*Quinone (or hydroquinone) found (mg)*	*% Error*
		Quinone		
1	33.24	6.138	6.108	—0.5
2	33.20		6.146	0.1
3	33.08		6.119	—0.3
4	33.20		6.124	—0.2
5	33.16		6.124	—0.2
			mean 6.124 ± 8	—0.2
		Hydroquinone		
1	33.24	6.252	6.254	0.0
2	33.29		6.270	0.4
4	33.20		6.249	—0.1
5	33.16		6.265	0.2
			mean 6.259 ± 8	0.1

The oxidation of hydroquinone by bromine was studied in the same solution by continuation of the back-titration. In this titration the indicator current rises as quinone is produced, and then decreases to a minimum. Past the equivalence point the indicator current again rises because the bromine–bromide couple behaves quasi-reversibly. Bromine was generated slightly past the e.p., and then back-titrated with +2 tin. Bromine does not add to the quinone ring, even at a two-fold excess under these conditions.

In the potentiometric titration of quinone with +2 tin the expected titration curve was obtained, with the equivalence point potential at +0.25 V *vs.* S.C.E. However, the potentiometric titration of hydroquinone with bromine is unsatisfactory, because there is no distinct potential change at the end-point. Because even in the titration of quinone long times were required for the establishment of steady potentials, amperometric end-point detection is preferable in both cases.

Typical results in Table V demonstrate that quinone and hydroquinone can be titrated with the stannous–bromine system with an average error of about ±0.2%.

ACKNOWLEDGEMENT

Appreciation is expressed to the National Science Foundation for a fellowship held by one of us (A.J.B.).

SUMMARY

The use of electrolytically generated +2 tin as a coulometric titrant has been studied. In a 3 to $4M$ sodium bromide and $0.2N$ hydrochloric acid solution, containing $0.2M$ stannic chloride, the generation of stannous ion is 100% efficient up to a current density of 80 mA/cm^2. With this medium iodine and bromine can be titrated coulometrically with errors of about ±0.3% or less. The titration is well suited for the iodometric determination of strong oxidants. Employing stannous ion and bromine for direct and reverse titrations, quinone and hydroquinone have been titrated.

RÉSUMÉ

On a étudié l'utilisation, pour les titrages coulométriques, de l'étain(II) électrolytiquement formé. On peut ainsi titrer l'iode et le brome et effectuer des dosages iodométriques d'oxydants forts.

ZUSAMMENFASSUNG

Es wird über coulometrische Titration mit Hilfe von elektrolytisch gebildetem Zinn-(II) berichtet. Beschrieben werden die Titrationen von Brom und Jod sowie die jodometrische Bestimmung starker Oxydationsmittel.

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A RAPID ROUTINE METHOD FOR THE DETERMINATION OF SUB-MICROGRAM AND MICROGRAM AMOUNTS OF BERYLLIUM IN FILTER PAPER

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INTRODUCTION

Due to the high toxicity of beryllium, and its increasing use as a nuclear material, the determination of traces of this element is growing in importance. A need exists for a rapid method for the routine determination of submicrogram quantities of beryllium. A method is presented in this paper which allows 20 filter paper smears to be analysed for beryllium in less than 6 hours.

Sodium hydroxide solutions of beryllium fluoresce strongly with 3,5,7,2′,4′-pentahydroxyflavone (Morin)[1]. This reaction provides by far the most sensitive chemical method at present available for the determination of beryllium[2]. Beryllium may be detected at a concentration as low as $5 \cdot 10^{-4}$ p.p.m., and $5 \cdot 10^{-3}$ p.p.m. may be measured with a precision comparable with normal spectrophotometric procedures. The method is, however, subject to many interferences[3], and a preliminary separation of beryllium is usually necessary. The separation has often been accomplished by precipitation of the beryllium as hydroxide or phosphate, using alumunium or iron carrier, followed by a mercury cathode electrolysis[2,4,5]. These procedures are too time-consuming for routine use. Several cation-exchange separations of beryllium have been described[6,7], and a method by NADKARNI, VARDE AND ATHAVALE[8], for the determination of beryllium in ores, was modified in this laboratory for use in the separation of trace amounts of this element. However, these cation-exchange procedures were rejected in favour of a more rapid anion-exchange separation from $9N$ hydrochloric acid. Many metals are retained by a strongly-basic anion-exchange resin from $9N$ HCl[9], whereas beryllium is not, and passes into the effluent. Most foreign elements which also escape the anion-exchange separation do not interfere, or their interference may be removed by complexing with ethylenediaminetetraacetic acid (EDTA).

APPARATUS

A Hilger "Uvispek" spectrophotometer with fluorimeter attachment was used for all fluorescence measurements. The exciting radiation is provided by a 36 W filament lamp, and the sample cells are of 18 ml capacity. A 365 mμ filter was used to isolate the exciting radiation.

Ion-exchange column

A simple U-tube type ion exchange column[10] was used, of length 11.4 cm and 0.64 cm in diameter while the lead-off capillary tube had an internal diameter of 0.32 cm. A glass-wool plug was used to support the resin, and a 50 ml separatory funnel was attached to the top of the column with a # B7 joint. The flow-rate was easily controlled by the stop-cock of the separatory funnel. This ion-exchange apparatus is very simple and cheap to construct, and it is convenient in routine work to have a number of such columns arranged in series, so that one column is available per sample.

Ion-exchange resin

De-acidite FF. From the Permutit Co., Ltd. London.

1% sodium stannite solution

Dissolve 1 g of stannous chloride dihydrate in 100 ml of 1.25N sodium hydroxide by warming gently on a water bath with continuous stirring. This solution must be prepared fresh daily.

0.025% Morin solution

B.D.H. grade 3,5,7,2′,4′ - pentahydroxyflavone was used without further purification. Dissolve 0.25 g in 1 l of 95% ethanol. Store in a refrigerator.

Quinine sulphate stock solution

Dissolve 0.125 g of quinine sulphate in 250 ml of water. Add 10 ml of 2N H_2SO_4 and dilute to 2 l. Store in a dark bottle.

All other chemicals used were of reagent grade.

PROCEDURE

Fill the ion-exchange column with water, then add De-acidite FF, as a slurry in water, until the column contains about 2 ml of resin. Place the separatory funnel in position and wash the resin first with 40 ml of water, then with 40 ml of 9N HCl.

Digest the filter paper smear in a small conical flask with 1 ml of HNO_3 and 4 ml of $HClO_4$. Evaporate to complete dryness on a hot plate. Dissolve the residue by warming with 10 ml of 9N HCl. Cool, and pass the solution through the ion-exchange column at a rate of 1–2 ml/min. Wash with 40 ml of 9N HCl and evaporate the effluent just to dryness. Dissolve the residue by warming with 5 ml water. Cool, and transfer to a 25-ml volumetric flask. Dilute to the mark with water.

Pipette a suitable aliquot of the sample solution into a small beaker. Dilute to about 25 ml with water. Add 1 ml of 10% EDTA (disodium salt) and neutralise carefully with 10% NaOH, using indicator paper. Transfer the solution to a 50-ml volumetric flask. Add 2 ml of sodium stannite solution, mix, then 1 ml of morin solution.

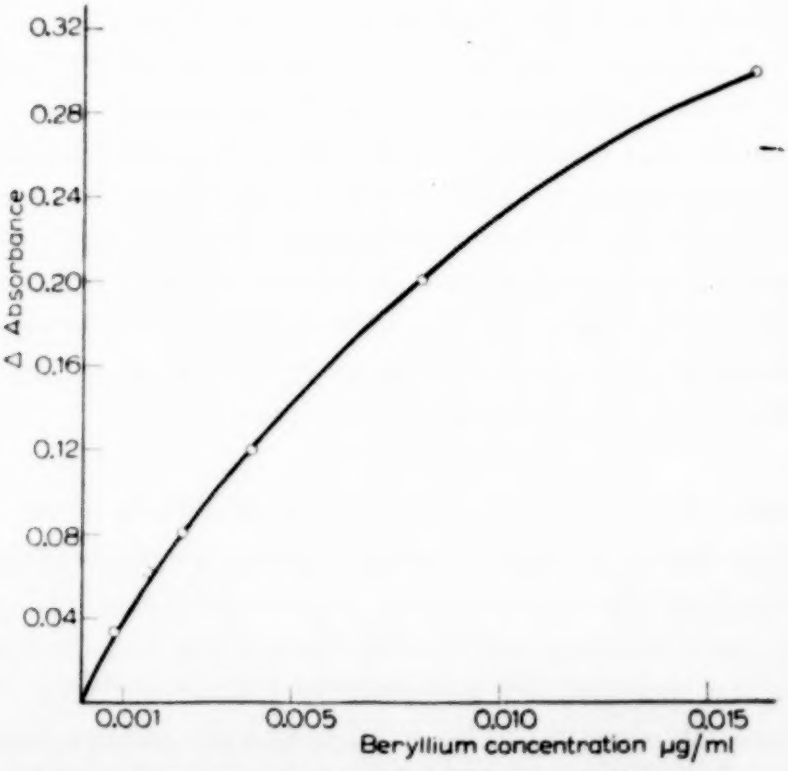

Fig. 1. Determination of beryllium with Morin.

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Dilute to volume with water. Prepare a blank in the same manner, substituting water for the sample aliquot. Dilute 2 ml of the quinine sulphate solution to 50 ml in a volumetric flask.

Determine the fluorescence after 15 min and before 60 min by setting the quinine sulphate solution at zero absorbance, then measuring the absorbance of the blank and sample solutions. The Δ absorbance value (blank absorbance minus sample absorbance) may then be related to beryllium concentration from a calibration curve (Fig. 1). The beryllium content of a blank filter paper, and of the acids used for digestion is usually less than 0.03 μg.

TABLE I

BERYLLIUM RECOVERY

Be taken (μg)	*Be found (μg)*	*% Recovery*
0.016	0.015	94
0.040	0.044	110
0.240	0.235	98
0.400	0.400	100
0.800	0.775	97
4.00	3.88	97

Beryllium recovery

Known amounts of beryllium were subjected to the ion-exchange separation. Table I shows that excellent recoveries may be obtained.

Sensitivity of the method

It may be seen from Fig. 1 that less than 0.05 μg of beryllium in a paper smear could be detected. LAITINEN AND KIVALO[5] recommend adding sodium sulphate or sodium chloride in a concentration of 1.5 to $2N$ to enhance the beryllium fluorescence. Sodium sulphate was found to be difficult to use at these concentrations, due to its relatively low solubility, and $1.5N$ sodium chloride, at the morin concentration used, actually depressed the fluorescence slightly. In addition, the fluorescence of solutions containing large concentrations of sodium chloride faded much faster than those without added salt. Using the procedure above, the fluorescence showed no appreciable fading for 60 min. A morin concentration of $5 \cdot 10^{-4}$ % in $0.05N$ NaOH was found to be optimum for maximum fluorescence.

Effect of diverse ions

Table II shows the effect of some common cations which were added to a known amount of beryllium and the determination carried out as in the procedure above.

It may be seen that thorium and chromium are the only serious interferences. Copper, zinc, iron and uranium are removed by the ion-exchange column. Calcium and nickel are effectively complexed by EDTA, and aluminium does not interfere in sodium hydroxide solution.

Thorium

Thorium is not retained by De-acidite FF from 9*N* HCl,[9] and does not form a strong complex with EDTA in alkaline solutions. If more than 500 μg of thorium is present in the final solution a precipitate of hydrated thorium oxide forms on the addition of sodium stannite reagent. Low results are then obtained, probably due to co-precipitation of beryllium. Smaller amounts of thorium do not precipitate, and the fluorescence of the solution is then enhanced, leading to high beryllium results. Using the recommended procedure, the maximum permissible concentration of thorium, for an error of less than 5%, is 80 times the beryllium concentration. The use of pyrophosphate, as recommended by SANDELL[3], did not remove the interference of thorium.

Chromium

Chromium interferes seriously, since chromite ion is formed in sodium hydroxide solution, and this appears to strongly absorb U.V. radiation. Chromium(III) was found to be only very weakly adsorbed on De-acidite FF from 9*N* HCl. Chromium (VI) is strongly adsorbed from 1–2*N* HCl, but is quantitatively reduced to the lower valency by 9*N* HCl. The maximum concentration of chromium permissible is 100 times the beryllium concentration.

TABLE II

EFFECT OF DIVERSE IONS

0.400 μg of Be taken in each case

Ion added	*Amount added mg*	*Be found μg*	*Relative error %*
Ca^{+2}	1.0	0.420	+5
Ni^{+2}	1.0	0.421	+5
Al^{+3}	1.0	0.385	−4
Cu^{+2}	1.0	0.377	−6
Zn^{+2}	1.0	0.388	−3
Pb^{+2}	1.0	0.400	0
Fe^{+3}	5.0	0.393	−2
U^{+6}	1.0	0.394	−2
Th^{+4}	1.0	0.248	−38
Th^{+4}	0.5	0.340	−15
Th^{+4}	0.1	0.520	+30
Th^{+4}	0.02	0.402	0
Cr^{+3}	0.5	0.041	−90
Cr^{+3}	0.25	0.128	−68
Cr^{+3}	0.05	0.387	−3

ACKNOWLEDGEMENT

It is a pleasure to acknowledge the assistance of Mr. D. B. IZARD with some of the experimental work.

SUMMARY

A rapid routine method for the determination of submicrogram and microgram amounts of beryllium in filter paper smears is presented. Beryllium is determined fluorimetrically with 3,5,7,2',4'-pentahydroxyflavone (Morin). Many interfering elements are removed by adsorption on a strongly basic anion-exchange resin from 9*N* hydrochloric acid.

RÉSUMÉ

Une méthode fluorimétrique rapide est proposée pour le dosage de traces de béryllium en utilisant la morine comme réactif. De nombreux ions gênants sont éliminés par adsorption sur une résine d'échange d'anions.

ZUSAMMENFASSUNG

Es wird eine fluorometrische Schnell-methode zur Bestimmung von sehr kleinen Mengen von Beryllium mit Hilfe von Morin als Reagens beschrieben. Eine grosse Anzahl störender Elemente können durch Behandlung mit einem Ionen-Austauscherharz entfernt werden.

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AMPEROMETRIC TITRATIONS WITH ROTATED PLATINUM ELECTRODE

I. DETERMINATION OF HYDRAZINE BY POTASSIUM BROMATE

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Amperometric titrations with a rotating platinum electrode have found several useful applications particularly in the determination of halides, cyanides and mercaptans employing silver nitrate and arsenic(III) and other materials employing potassium bromate as reagents[1]. Laitinen and Kolthoff[2] first studied the amperometric titration of trivalent arsenic with potassium bromate in solution $1.0N$ in hydrochloric acid and $0.05M$ in potassium bromide. During the titration the current remains practically zero but increases linearly after the end-point due to the liberation of free bromine by the interaction of excess bromate and bromide:

$$BrO_3^- + 5Br^- \rightarrow 3Br_2 + 3H_2O$$

Hypobromite has also been used for this purpose. The arsenite–bromate reaction was later extended to antimony(III), ammonia and such organic compounds which react rapidly with bromine through substitution or addition. The principal advantages of amperometry at rotating platinum electrode are the feasibility of performing titrations in presence of oxygen and the immediate attainment of steady current values.

Potassium bromate is a powerful oxidizing agent in acidic medium and the titrations are generally performed in the initial presence of bromide. Methyl orange, indigo or other dyestuffs are destroyed by free bromine and serve therefore as irreversible indicators. Reversible indicators, like *p*-ethoxychrysoidine were later discovered and found satisfactory. In general, the indicator errors in bromatometry become appreciable in very dilute solutions and offer therefore a limitation to this titrimetric method of analysis. Under these circumstances, amperometric end-point becomes ideally suitable[3].

Hydrazine is oxidized quantitatively to nitrogen by bromate[4]:

$$3N_2H_4 + 2HBrO_3 \rightarrow 3N_2 + 2HBr + 6H_2O$$

The titration is performed in a 20% hydrochloric acid solution using indigo as indicator[5]. SZEBELLEDY AND MADIS[6] proposed phosphomolybdic acid as indicator in the absence of mineral acids.

In the present work a detailed study has been undertaken to investigate the suitability of and the optimum conditions in employing amperometric end-point in the determination of hydrazine by potassium bromate.

EXPERIMENTAL

Reagents

Analytically pure hydrazine sulfate and potassium bromate were used to prepare their aqueous solutions. The hydrazine content was ascertained by titration with bromate using *p*-ethoxychrysoidine indicator and also with iodate using chloroform as indicator. Low concentration hydrazine sulfate and bromate solutions were obtained by successive dilution. All the other chemicals used were of the reagent grade.

Apparatus

Sargent's compact unit "Ampot", consisting of dry cell batteries as voltage source, a voltage indicator (0–3 V), and a microammeter (0–20 μA), was used as the amperometric instrument. The microammeter had appropriate shunting resistors for increasing full scale capacity by factors of 1, 2, 4 and 10. A 'safe' position shorts the meter and protects it during preliminary connections and voltage adjustment. A ten-turn potentiometer with dial calibrated in one-thousand units helps in adjusting the applied e.m.f. accurately. The indicator electrode consisted of a piece of platinum wire, 6 to 8 mm in length and 0.5 mm in diameter, sealed into the side of a small bulb blown at the end of a glass tubing. The electrode was rotated at a constant speed of 600 r.p.m. by means of a Bodine motor supplied by Sargent for this purpose. Fischer's saturated calomel electrode served as reference and it was connected to the titrating solution through agar-saturated potassium chloride bridge. Titrations were carried out in a tall beaker of about 150-ml capacity.

Procedure

To an aliquot portion of hydrazine sulfate transferred into the titration beaker, a sufficient quantity of hydrochloric acid to maintain its overall normality 2*N* and 10 ml 0.5*M* potassium bromide solution were added, and the total volume brought to 100 ml with water. The rotating platinum electrode was made the cathode and the saturated calomel the anode. The current multiplier switch was kept in the lowest multiplier position and no external e.m.f. was applied across the electrodes. The initial current, which was generally slightly more than zero, was noted and the titration commenced with 0.1*N* $KBrO_3$. After the end-point 6–8 increments of 0.05 or 0.1 ml of the reagent were added and the current measured. For smaller quantities of hydrazine, 0.01 or 0.001 N bromate was used and the current measured at multiplier position of 2 or 1. A plot of the reagent volume added *versus* the current in microamperes results in a reversed L-type of graph and gives the experimental end-point.

A typical titration curve is shown in Fig. 1 and a representative set of data for the estimation of hydrazine is entered in Table I. It will be seen that the experimental results are in close agreement with those anticipated on the basis of standard method using iodate or bromate.

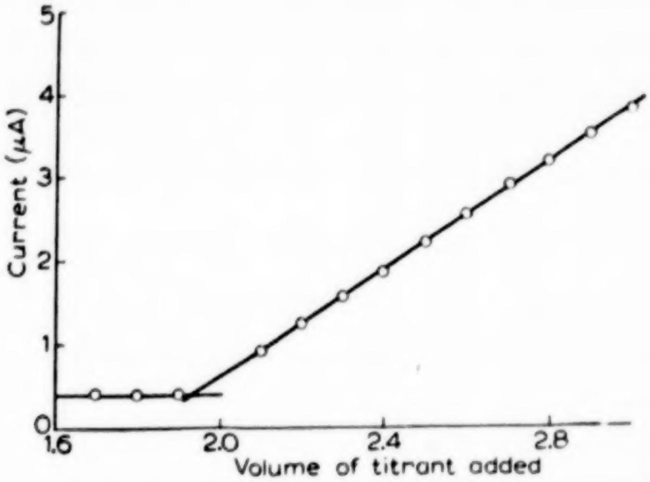

Fig. 1. Amperometric titration of 5 ml $0.9940 \cdot 10^{-3} M$ hydrazine sulfate with $0.01027 N$ $KBrO_3$
End-point: theoretical 1.9325 ml; from graph 1.935 ml.

TABLE I

DETERMINATION OF HYDRAZINE BY POTASSIUM BROMATE

Hydrazine sulfate molarity, M	*Hydrazine, mg*		*Difference mg*
	Calculated	*Found*	
$0.9915 \cdot 10^{-1}$	3·177	3·152	0.027
$0.9940 \cdot 10^{-2}$	1.593	1.588	0.005
$0.9940 \cdot 10^{-2}$	0.6372	0.6420	0.0048
$0.9940 \cdot 10^{-2}$	0.3186	0.3210	0.0024
$0.9940 \cdot 10^{-3}$	0.09558	0.09547	0.0011
$0.9940 \cdot 10^{-3}$	0.06372	0.06336	0.0036
$0.9940 \cdot 10^{-3}$	0.03186	0.03210	0.00024
$0.9940 \cdot 10^{-4}$	0.01593	0.01678	0.00085
$0.9940 \cdot 10^{-4}$	0.003186	0.003360	0.000174

DISCUSSION

A series of experiments carried out to study the influence of acidity on the oxidation of hydrazine by bromate revealed that the titration could be performed accurately in an overall concentration of hydrochloric acid maintained between 0.5 and 4N (see Table II). In the ordinary titrations with indicator, a minimum hydrochloric acid content of 2N is recommended while in the SZEBELLEDY-MADIS procedure interference is caused by the presence of mineral acids. At lower concentrations of hydrochloric acid than 2N, hydrazine tends to undergo side reactions such as the formation of hydrazoic acid and ammonia[3]. Quantitative results at an acidity as low as 0.5N hydrochloric acid in the present work may be attributed to the inherent difference in

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TABLE II

EFFECT OF HYDROCHLORIC ACID CONCENTRATION

Overall normality of HCl, N	*Hydrazine, mg*	
	Calculated	*Found*
0.5	0.1593	0.1588
0.5	1.593	1.588
1.0	0.1593	0.1588
1.5	0.1593	0.1588
2.0	0.1593	0.1588
3.0	0.1593	0.1588
4.0	0.1593	0.1588
4.0	1.593	1.588

amperometry and the titration using indicators. In the latter, titration before and near the end-point is performed slowly — a circumstance in which hydrazine is susceptible towards side reactions. In amperometric titration, however, a slight excess of bromate is added which converts hydrazine rapidly to nitrogen and the current readings corresponding to the increments of bromate only after the end-point are of significance. No systematic study seems to have been made using sulfuric in place of hydrochloric acid in the oxidation of hydrazine by bromate. Accurate results were obtained when the total sulfuric acid concentration was adjusted between 1 and 5*N* (see Table III). This reaction appears to be slightly slower than in hydrochloric acid.

The initial presence of bromide in the system helps in eliminating the first stage of bromate reaction, $BrO_3^- + 6H^+ + 6e^- \rightarrow Br^- + 3H_2O$, so that only the second reaction, $BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$, is involved. In conformity with earlier observations by LAITINEN AND KOLTHOFF[2] on the arsenite–bromate reaction, an optimum overall concentration of 0.05*M* potassium bromide is preferable. Larger quantities of bromide have, however, little adverse effect.

TABLE III

EFFECT OF SULFURIC ACID CONCENTRATION

Overall normality of H_2SO_4, N	*Hydrazine, mg*	
	Calculated	*Found*
1.0	0.1593	0.1588
1.0	1.593	1.588
2.0	0.1593	0.1588
3.0	0.1593	0.1588
4.0	0.1593	0.1588
5.0	0.1593	0.1588
5.0	1.593	1.588

The amperometric titration of hydrazine with bromate can be effected at an applied potential between 0 and 0.3 *V versus* the S.C.E. It is, however, simple to perform the titration at an applied external e.m.f. of zero.

The optimum conditions for the amperometric determination of hydrazine by bromate are: 2*N* hydrochloric acid, 0.05*M* potassium bromide and an applied e.m.f.

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of zero *versus* S.C.E. By adjusting the bromate concentration about ten times of hydrazine the volume changes will be negligible. For very precise work and when handling smaller volumes, it is advisable to apply volume correction as follows[7]:

$$i_{\text{corr.}} = i_{\text{meas.}} \left(\frac{V + v}{V}\right)$$

where V denotes the original volume of the solution titrated and v the reagent volume added at any point. Under the given experimental conditions, it was possible to titrate $1 \cdot 10^{-1}$ to $1 \cdot 10^{-3} M$ hydrazine sulfate solution corresponding to about 0.03–3 mg of hydrazine within a very reasonable accuracy. At higher dilutions of the order of $1 \cdot 10^{-4} M$ and containing about 3 μg hydrazine, the titration could still be performed but with an error of nearly 5%. At such low concentrations of hydrazine, titrations either with indicator or by other electrometric methods do not yield trustworthy results. It may be pointed out that the present amperometric method particularly for the micro-estimation of hydrazine by standard $KBrO_3$ is accurate, rapid, and simple besides being independent of visual color changes.

Further work on the bromatometric determination of phenylhydrazine, semicarbazide and other oxidizable materials on similar lines is in progress.

ACKNOWLEDGEMENT

We are indebted to Boyd Professor Dr. PHILIP W. WEST for research facilities and interest in the work.

SUMMARY

The reaction between hydrazine and potassium bromate is studied amperometrically at rotating platinum electrode. The bromate titration is performed at an applied e.m.f. of zero (*versus* S.C.E.) and in the presence of bromide and 1–5N sulfuric acid or 0.5–4N hydrochloric acid. Quantities ranging from 30 μg to 3 mg of hydrazine can be estimated accurately by this method. Determination of phenylhydrazine, semicarbazide and other oxidizable materials on similar lines is suggested.

RÉSUMÉ

On a étudié la réaction entre l'hydrazine et le bromate de potassium, par ampérométrie, au moyen d'une électrode de platine tournante. L'hydrazine peut ainsi être dosée avec précision. Un dosage est proposé pour la phénylhydrazine, la semicarbazide et d'autres substances analogues.

ZUSAMMENFASSUNG

Die Reaktion zwischen Hydrazin und Kaliumbromat wurde amperometrisch mit Hilfe einer rotierenden Platinelektrode untersucht. Nach dieser Methode lässt sich Hydrazin sehr genau bestimmen. Ihre Anwendungsmöglichkeit bei Phenylhydrazin, Semicarbazid und anderen ähnlichen Verbindungen wird geprüft werden.

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THE AMPEROMETRIC AND CONSTANT CURRENT POTENTIOMETRIC TITRATION OF ETHYLENEDIAMINETETRAACETIC ACID WITH COPPER (II)

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PRIBIL AND MATYSKA[1], ACKERMANN AND SCHWARZENBACH[2], AND REILLY, SCRIBNER, AND TEMPLE[3] reported the amperometric titration of ethylenediaminetraacetic acid (EDTA) with copper(II) at the dropping mercury electrode. TANAKA, KODAMA, SASKI, AND SUGINO[4] titrated copper with EDTA in an acetate buffer of pH 4.2 using the dropping mercury electrode.

NIKELLEY AND COOKE[5] used the mercury-pool indicator electrode for the EDTA titration of micromolar solutions of copper. In favorable cases, titrations were successfully carried out at concentrations approaching $10^{-7}M$.

PRIBIL, KOUDELA, AND MATYSKA[6] used a platinum–calomel electrode pair to titrate copper(II) by adding a known quantity of EDTA and back-titrating the excess with iron(III). BELCHER, GIBBONS, AND WEST[7] have shown that copper could be titrated directly with EDTA using this electrode system. POLYAK[8] has applied this electrode system to the determination of copper in electrolyte baths.

SIGGIA, EICHLIN, AND RHEINHART[9] used the platinum–calomel and the mercury coated platinum–calomel electrode pairs to titrate $0.1M$ copper with EDTA.

REILLEY[10] proposed the use of a mercury electrode for the potentiometric end-point detection in EDTA titrations. SADEK AND REILLEY[11] adapted the mercury electrode method to ultramicro chelometric titrations. The mercury electrode was also employed by POLCIN[12] for the EDTA titration of copper. SAJO[13] used zinc as the back-titrant for the potentiometric determination of copper.

Bimetallic electrode systems also have been employed. BUDANOVA AND PLATONOVA[14] have reported the determination of copper by adding excess EDTA and back-titrating with lead ions using the platinum–tungstan system.

Copper(II) was titrated automatically by HASLAM, SQUIRRELL, AND HESKINS[15] using disodium dihydrogen ethylenediaminetetraacetate. The end-point was taken as the point where the pH did not change upon further addition of the titrant.

NIGHTINGALE[16] reported the potentiometric titration as small constant current of EDTA with copper using the platinum electrode.

KOLTHOFF[17] proposed the amperometric titration of ethylenediaminetetraacetic acid with copper(II) at the rotated platinum electrode. The rotated platinum electrode is more desirable then a dropping mercury electrode as an indicator electrode because of its convenience in handling and greater sensitivity.

The amperometric titration proposed by KOLTHOFF and the constant current potentiometric titration of NIGHTINGALE, both using the rotated platinum electrode as indicator electrode, were tried in an acidic solution, rather than in basic solutions used by the majority of the above researchers.

MATERIALS

Standard copper(II) solutions were prepared by solution of No. 18 electrolytic copper wire obtained from the Melins Co., Cleveland, Ohio, in a minimum amount of nitric acid, followed by dilution to volume.

Standard solutions of EDTA were prepared by dissolving "Baker Analyzed" disodium dihydrogen ethylenediaminetetraacetate dihydrate obtained from the J. T. Baker Chemical Co., Phillipsburg, N.J., in water and standardizing against standard copper using Murexide as an indicator.

All chemicals were reagent grade.

APPARATUS

The Sargent Manual Polarograph, Model III, made by E. H. Sargent and Co., Chicago, Ill., and a manual polarograph constructed in the Rensselaer Polytechnic Institute Chemistry Department were used. The rotated platinum wire micro electrode was made of No. 18 platinum wire with 0.5 cm exposed to solution. It was driven at 600 r.p.m. by a Sargent Synchronous Motor, Type KYC-22.

Potentials were measured with a Triplett Model 620 VTVM, Serial No. 6691. The current for the constant current potentiometric titrations was supplied through a large series resistor by a 1½-V battery.

PROCEDURE

Polarograms of the copper–EDTA titration were run in a $0.2 M$ acetate buffer of pH 5.0 at different points in the titration using the rotated platinum micro electrode (R.P.E.) *versus* the saturated calomel electrode (S.C.E.) with the manual polarograph built at Rensselaer Polytechnic Institute. Typical polarograms are shown in Fig. 1, where A is 50% to end-point, B is 1% before end-point, and C is 1% after end-point in the titration of EDTA with Cu(II). The solutions were degassed with a glass-frit bubbler for 15 min with nitrogen before each polarogram and continously during the polarogram. For all experiments, the platinum electrode was cleaned by washing with conc. nitric acid and then placed in distilled water and shorted to the S.C.E. until no current flowed through the circuit formed.

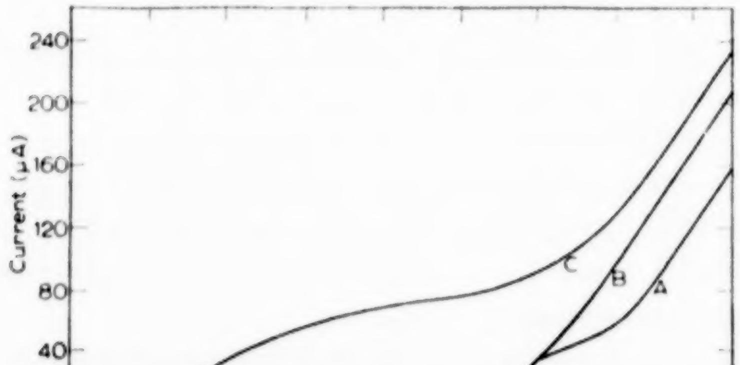

Fig. 1. Polarograms of Cu–EDTA titration.

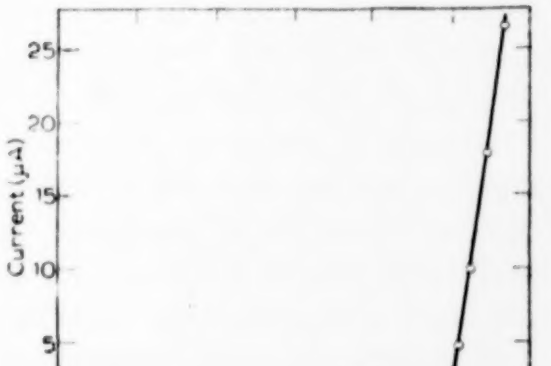

Fig. 2. Amperometric titration of EDTA.

The amperometric titration of EDTA with copper(II) was performed in a 100-ml beaker containing 50 ml of buffer and 10 ml of EDTA solution using the R.P.E. at an applied potential of about -0.45 V *vs.* S.C.E.

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The solutions were degassed with a glass-frit bubbler for 15 min with nitrogen before each titration and continously during the titration. The titrant was added in 1-ml increments before the end-point region and 0.2-ml increments in and after the end-point region. In all titrations, except the last three sets of data where two minute intervals were used, one minute intervals were taken between addition of reagent and reading of current. The constant potential was supplied by and the current was read with the manual polarograph built at Rensselaer Polytechnic Institute except for the last three sets of data where the Sargent Manual Polarograph was used.

A typical amperometric titration graph is shown in Fig. 2 .The end-point was taken as the intersection of the two straight lines.

The potentiometric titration at small constant current of EDTA with copper(II) was performed in a 100 ml beaker containing 50 ml buffer and 10 ml of EDTA solution using the R.P.E. *vs.* S.C.E. The solution was degassed with nitrogen dispersed through a glass-frit bubbler for 15 min before each experiment and continously during the titration. The titrant was added in 2-ml increments before the end-point region and in 2-drops increments in the end-point region. In all titrations, one minute intervals were taken between addition of reagent and reading of potential. The constant current was supplied by $1\frac{1}{2}$-V battery, and the potential was read with the Triplett VTVM.

A typical constant current potentiometric titration graph is shown in Fig. 3. The end-point was determined either from the inflection point on a graphical plot or by interpolation between readings at the point of steepest potential break.

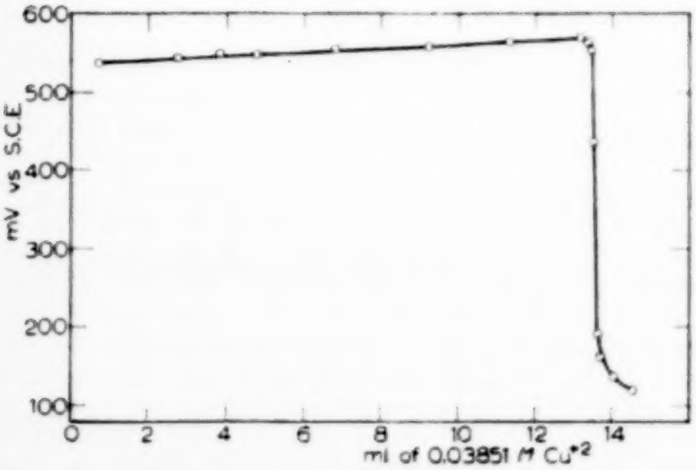

Fig. 3. Potentiometric titration of EDTA.

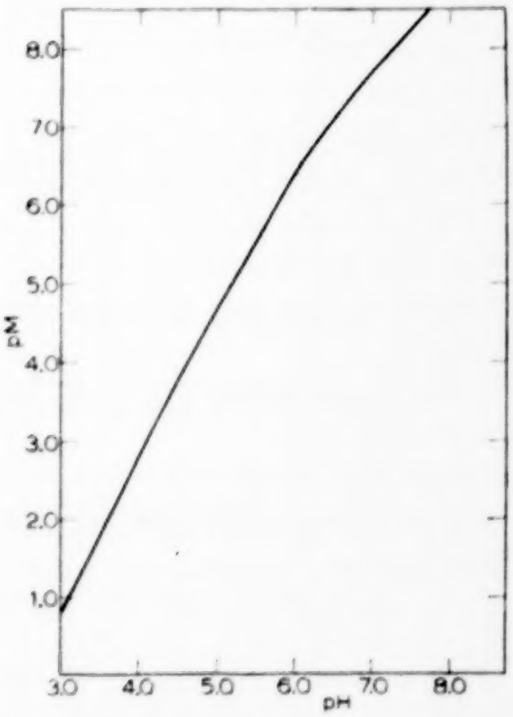

Fig. 4. pM *vs.* pH.

RESULTS

The experimental results are given in Tables I and II.

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TABLE I

AMPEROMETRIC TITRATION

App. pot.(—E) (V)	*Taken (μequiv.)*	*No. of det.*	*Found (μequiv.)*	*S.D. (%)*	*Buffer*	*pH*
0.50	983.6	5	981.2	0.20	0.1 M acetate 0.1 M KNO_3	5.0
	983.6	2	980.1	0.20		5.0
0.45	717.0	8	718.5	0.64	0.2 M acetate	5.0
	983.6	6	983.2	0.30		5.0
	358.5	6	358.7	0.50		5.0
	179.2	6	179.0	0.67		5.0
	98.4	2	97.8	0.70		4.73
	98.4	2	98.1	0.70		5.73
	49.2	4	49.2	0.41		5.0
	9.84	4	9.84	0.41		5.0
	0.984	2	0.801	N.D.		5.0

TABLE II

CONSTANT CURRENT POTENTIOMETRIC TITRATION

App. current (μA)	*Taken (μequiv.)*	*No. of det.*	*Found (μequiv.)*	*S.D. (%)*	*Buffer*	*pH*
5	983.6	5	984.3	0.12	0.2 M acetate	5.0
2	245.9	6	246.0	0.40		5.0
	98.4	6	98.2	0.20		5.0
1	49.2	6	48.9	0.20		5.0

DISCUSSION

The experimental results for the amperometric titration show that this titration can be used to titrate from 983.6 down to 9.84 μequiv. of EDTA in about 70 ml of solution with copper(II) at the R.P.E. in an acetate buffer of pH 5.0 These amounts correspond to a concentration range of $7 \cdot 10^{-3}$ to $7 \cdot 10^{-5} M$ EDTA. The results also show that when 98.4 μequiv. were taken ($7 \cdot 10^{-4} M$ EDTA), a pH of 4.73 and 5.73 did not change the amount of EDTA found to a significant degree.

When 0.984 μequiv. ($7 \cdot 10^{-6} M$) of EDTA were titrated in an acetate buffer of pH 5.0, the amount found did not compare well with the amount taken because the EDTA at this low concentration and at this pH does not completely complex the copper.

The stability constant, K, for the fundamental reaction

$$Cu^{+2} + Y^{-4} \rightleftarrows CuY^{-2}$$

where Cu^{+2} is the copper(II) ion and Y^{-4}, the fully ionized ethylenediaminetetraacetate ion, is

$$K = (CuY^{-2}) / (Cu^{+2}) (Y^{-4}).$$

The stability constant for the copper–EDTA complex is $10^{18.8}$. The apparent stability constant at a particular pH may be calculated by dividing K by α, the fraction of EDTA which is present as Y^{-4} (and not as other dissociated states of H_4Y).

$\alpha = 1 + (H^+) / K_4 + (H^+)^2 / K_4K_3 + (H^+)^3 / K_4K_3K_2 + (H^+)^4 / K_4K_3K_2K_1$ where K_4, K_3, K_2, and K_1 are the acidity constants of EDTA.

References p. 485

Since a concentration less than about $7 \cdot 10^{-5} M$ EDTA could not be titrated at a pH of 5.0, the above equations were used to calculate a complexed copper to uncomplexed copper ratio, at the end-point, below which the titration would not go to completion. This ratio was found to be 10^4. Using this ratio, the minimum concentration of EDTA that could be titrated with copper(II) (or *vice versa*) at a given pH was determined for several pH values. These values are plotted in Fig. 4 as log of minimum concentration, pM, *versus* pH.

The experimental results for the potentiometric titration at small constant current of EDTA with copper(II) at the R.P.E. show that this titration can be used to determine 983.6 to 49.2 μequiv. of EDTA in about 70 ml of solution ($7 \cdot 10^{-3}$ to $3.5 \cdot 10^{-4} M$ EDTA). In all experiments, a very sharp potential break of about 0.3 V occurred at the end-point.

An applied current of 5 μA may be a little high for titrating below about 500 μequiv. in 70 ml of solution since the amount of free copper(II) required to give a diffusion current of this size is a little beyond the end-point and will be further beyond the end-point as the concentration of EDTA in solution is decreased in subsequent titrations. An applied current of 1-2 μA is recommended.

SUMMARY

The amperometric titration of $7 \cdot 10^{-5} M$ EDTA with copper(II) was performed in an acetate buffer of pH 5.0 at the rotated platinum electrode. A pH range of 4.73 to 5.73 was used to titrate $7 \cdot 10^{-4} M$ EDTA. The potentiometric titration at small constant current of $7 \cdot 10^{-3}$ to $3.5 \cdot 10^{-4} M$ EDTA with copper(II) was performed in an acetate buffer of pH 5.0 at the rotated platinum electrode.

RÉSUMÉ

Un titrage ampérométrique et un titrage potentiométrique de l'acide éthylènediaminotétra acétique, par le cuivre(II), ont été effectués en milieu tampon à l'électrode tournante de platine.

ZUSAMMENFASSUNG

Es wird eine amperometrische und potentiometrische Titration von Äthylendiaminotetraessigsäure mit Cu-(II) in gepufferter Lösung an einer rotierenden Platinelektrode beschrieben.

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EFFECT OF GELATIN AND POLYOXYETHYLENE LAURYL ETHER ON POLAROGRAPHIC DIFFUSION CURRENTS OF SOME INORGANIC IONS*

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In polarography, some surface-active substances are generally used to suppress the maximum in the current–voltage curve. Gelatin has been known as one of the best maximum suppressors. Although gelatin is very effective and widely used for this purpose, it has a disadvantage that the addition of gelatin of relatively high concentration decreases the diffusion current of many electroactive species. Furthermore, gelatin is rapidly deteriorated and its stock solution must be renewed quite frequently. In order to overcome these deficiencies of gelatin, the use of certain kinds of synthetic detergents as a maximum suppressor has been widely examined[1], and polyoxyethylene lauryl ether (LEO), which is a non-ionic detergent, has been expected to be very useful in the polarographic analysis[2].

The effect of gelatin on the diffusion current was already reported by some investigators and was explained by assuming the combination between electroactive species and gelatin molecules[3,4]. This evidence was also applied to the study of the interaction of electroactive species with gelatin molecules[5,6]. However, no systematic study on the effect of gelatin on diffusion currents at the conventional dropping mercury electrode (DME) has been found in the literature. In this paper, the effect of gelatin and LEO on the diffusion currents of several inorganic reducible ions is presented, and the potentiality of LEO as a maximum suppressor is discussed.

APPARATUS AND REAGENTS

Current–voltage curves were measured either by a Shimadzu RP-II pen-recording polarograph or by a manual polarograph[7], the latter of which was used for the accurate determination of the diffusion current. A mercury pool electrode of a large area in a saturated potassium chloride solution connected to the cell solution by a HUME AND HARRIS-type salt bridge[8] was employed as the anode, and a saturated calomel electrode was used as a reference electrode to measure the electrode potential of the DME. The drop time and the rate of flow of mercury of the DME were measured under the same conditions as those in the determination of diffusion current constants.

The differential capacity of the DME was measured by an impedance bridge similar to that of GRAHAME[9]. The balance of the bridge was determined just before the detachment of the mercury drop from the tip of the capillary. In this case, the DME of relatively long drop time was used. Its drop time and rate of flow of mercury were 8.62 sec and 0.906 mg/sec, respectively, in an air-free 0.1 M potassium nitrate solution at −0.5 V *vs.* S.C.E.

The relative viscosity of the solution was measured by using a U-type Ostwald viscosimeter, through which 10.0 ml of distilled water flowed in 39.5 sec at 25°.

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All measurements were carried out in a thermostat of 25.0 ± 0.1°.

The standard solutions of cadmium and zinc were prepared by dissolving known amounts of pure cadmium and zinc metals in distilled nitric acid and hydrochloric acid, respectively. The sample of LEO of high purity was kindly prepared by Nedzu Chemical Laboratory, Tokyo; it has a chemical formula of $C_{12}H_{25}O(C_2H_4O)_nOH$, where n is about 15*. All other chemicals were of analytical reagent grade, and redistilled water was used to prepare the solutions of the desired concentration. The stock solution of ferric ammonium sulfate was kept in a brown bottle, and the polarographic measurement of trioxalatoferrate(III) ions was carried out in a cell made of brown glass.

RESULTS AND DISCUSSION

Adsorbability and maximum suppression point of LEO

It is necessary that a maximum suppressor be adsorbed on the surface of the DME over a wide range of the electrode potential. The previous paper[2] showed from the experimental results on the electrocapillary curve that LEO is very surface-active in 0.1*M* potassium chloride solution. The adsorption of LEO on the DME in 0.1*M* potassium nitrate solution was also studied by measuring the differential capacity of the electrode at various electrode potentials, some results of which are shown in Fig. 1. In general, the capacity, measured at the ordinary DME, of such a substance of relatively large molecular weight as LEO can not be considered as that corresponding to the equilibrium state of the adsorption.[10] However, it can be concluded from the results in Fig. 1 that LEO strongly adsorbs on the surface of the DME over the potential range from 0 to −1.6 V *vs.* S.C.E. in 0.1*M* potassium nitrate solution.

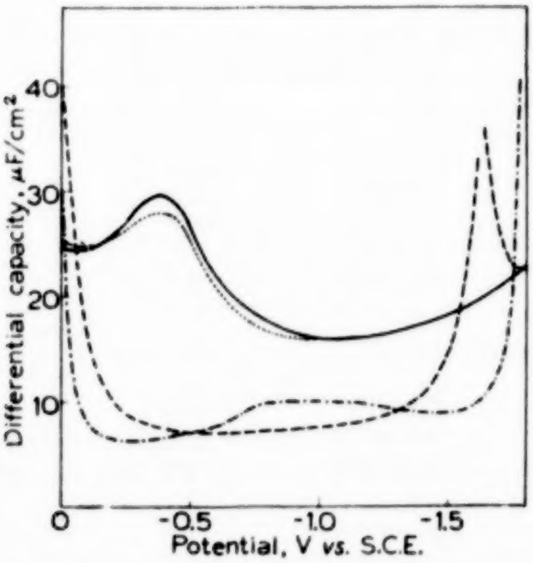

Fig. 1. Differential capacity of LEO solutions containing 0.1*M* KNO_3 at 25°: —, 0.1*M* KNO_3; . . ., $2\cdot10^{-6}M$ LEO; — —, $5\cdot10^{-4}M$ LEO; —.—, $1\cdot10^{-3}M$ LEO.

The ability of surface-active substances to suppress the maximum can be conveniently examined by measuring their maximum suppression points (MSP)[11] for various electroactive species. The MSP is defined as the minimum concentration of the surface-active substance which is necessary to make the maximum current, i_m, equal to the limiting (diffusion) current, i_l; it was determined graphically by plotting i_m/i_l against the logarithm of the concentration of the surface-active substance. The MSP's of LEO for some reducible ions are shown in Table I. It was found that the MSP's of LEO generally increase with the increase of the concentration of reducible ions or with the decrease of the concentration of indifferent electrolytes (Tables II and III).

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* A similar sample can be obtained from Nikko Co., Tokyo, under the trade name of "Nikkol BL-10".

TABLE I

MSP's OF LEO FOR SOME REDUCIBLE IONS

Reducible ions	*MSP, M*
1 m*M* Cu(II) in 0.1*M* KNO_3	$4.1 \cdot 10^{-5}$
3 m*M* Pb(II) in 0.1*M* KCl[a]	$1.3 \cdot 10^{-6}$
3 m*M* Ni(II) in 0.1*M* KCl[a]	$1.0 \cdot 10^{-6}$
1 m*M* Co(II) in 0.1*M* KCl	$1.2 \cdot 10^{-6}$

[a] Data from ref. [2].

TABLE II

MSP's OF LEO FOR VARIOUS CONCENTRATIONS OF COPPER(II) AND COBALT(II) IONS

Cu(II)[a]		*Co(II)*[b]	
Concn. of Cu(II) ion mM	*MSP M*	*Concn. of Co(II) ion mM*	*MSP M*
0.6	$2.7 \cdot 10^{-6}$	0.4	$2.5 \cdot 10^{-7}$
0.8	$5.2 \cdot 10^{-6}$	0.5	$6.5 \cdot 10^{-7}$
0.9	$1.1 \cdot 10^{-5}$	1.0	$1.2 \cdot 10^{-6}$
1.0	$4.1 \cdot 10^{-5}$	1.2	$1.4 \cdot 10^{-6}$
2.0	$1.1 \cdot 10^{-4}$	2.5	$3.2 \cdot 10^{-6}$
3.0	$1.6 \cdot 10^{-4}$	3.8	$4.1 \cdot 10^{-6}$
5.0	$2.0 \cdot 10^{-4}$	7.5	$7.0 \cdot 10^{-6}$

[a] In 0.1*M* potassium nitrate solution.
[b] In 0.1*M* potassium chloride solution.

TABLE III

MSP's OF LEO FOR 0.3 m*M* OF COPPER(II) AND COBALT(II) IONS IN VARIOUS CONCENTRATIONS OF INDIFFERENT SALTS

Concn. of indifferent salts M	*MSP, M*	
	Cu(II)[a]	*Co(II)*[b]
0.03	$3.2 \cdot 10^{-6}$	$2.4 \cdot 10^{-6}$
0.05	$1.4 \cdot 10^{-6}$	$1.1 \cdot 10^{-6}$
0.1	$8.5 \cdot 10^{-8}$	$1.7 \cdot 10^{-7}$
0.2	0	$3.1 \cdot 10^{-8}$
0.3	0	0

[a] In potassium nitrate solution.
[b] In potassium chloride solution.

It can be concluded from these experimental results that many polarographic maxima of the first kind are effectively suppressed by the addition of LEO less than $1 \cdot 10^{-5} M$. In the case of copper-maximum in $0.1 M$ potassium nitrate solution, however, the MSP of LEO is relatively high, i.e., of the order of 10^{-5} to $10^{-4} M$. This may be attributed to the fact that the potential, where the maximum of copper ion appears, is almost identical with the desorption potential of LEO in the positive branch of the electrocapillary curve (Fig. 1).

Effect of gelatin and LEO on current–voltage curves

The presence of surface-active substances generally increases the overpotential of the electrode reaction and distorts the shape of the current–voltage curve. Some experimental results on the effect of surface-active substances on the polarographic current–voltage curve were reported in the previous paper[2]. In the case of copper(II) ions in $0.1 M$ potassium nitrate solution, a minimum of the current appeared in the potential region of the electrocapillary maximum, when the concentration of LEO or gelatin was higher than 0.05 mM or 0.02%, respectively (Fig. 2). Similar phenomena were also observed in the polarographic reduction of trioxalatoferrate(III) ions in $0.5 M$ potassium oxalate solution, which contradicts HEYROVSKY's theory on the electrode reaction to the effect that the electrode reaction involving only one electron in the electron-transfer process is not affected by the presence of surface-active substances[12]. The effect of LEO on the electrode reaction was found to be larger than that of gelatin in all cases. These results can be reasonably explained by assuming the retardation of the electrode reaction due to the presence of the adsorbed film of surface-active substances on the surface of the DME[13]. The details will be discussed elsewhere.

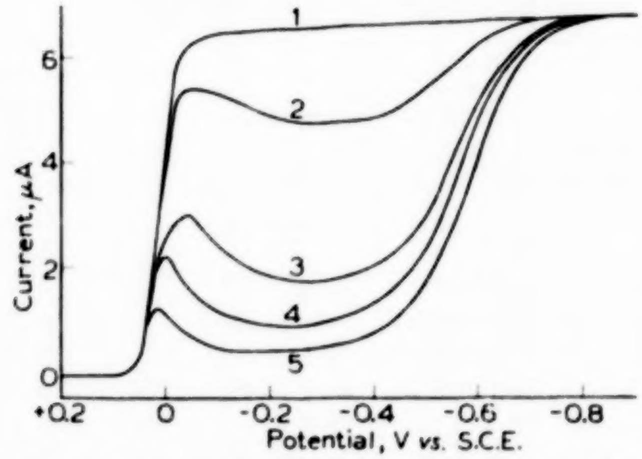

Fig. 2. Effect of LEO on the polarographic reduction wave of 1 mM Cu(II) ion in $0.1 M$ KNO_3 solution: 1, $2 \cdot 10^{-5} M$; 2, $5 \cdot 10^{-5} M$; 3, $1 \cdot 10^{-4} M$; 4, $2 \cdot 10^{-4} M$; 5, $1 \cdot 10^{-3} M$ LEO.

Effect of gelatin and LEO on diffusion currents

Diffusion current constants, I, of some metal ions were determined in the solution containing various concentrations of gelatin or LEO by using the relation[14]:

$$I = \frac{i_d}{C\, m^{2/3}\, t^{1/6}}$$

where i_d is the diffusion current in μA, C the bulk concentration of the reducible ion in mM and m and t are the rate of flow of mercury in mg/sec and the drop time in sec, respectively, at the electrode potential where i_d is measured. An example of the experimental data is presented in Table IV. Tables V and VI clearly indicate that the presence of gelatin generally decreases the value of diffusion current constants when its concentration is higher than 0.05%, while the presence of LEO does not change the value of diffusion current constants over the wide concentration range of LEO.

The effect of viscosity of the solution must be considered as one of the reasons for the change of diffusion current constants[15]. The relative viscosity of 0.1 M potassium nitrate solution containing 1 mM LEO was found to be only 0.4% larger than that of 0.1M potassium nitrate solution. On the other hand, the addition of 0.4% gelatin increased the relative viscosity of 0.1M potassium nitrate solution about 19% as shown in Table VII. However, it has been known that the change of viscosity of the solution due to the presence of lyophilic colloids such as gelatin does not affect the

TABLE IV

DIFFUSION CURRENTS, DIFFUSION CURRENT CONSTANTS AND CHARACTERISTICS OF THE DME IN THE SOLUTION CONTAINING 1.00 mM CADMIUM ION, 0.1M POTASSIUM NITRATE AND VARIOUS CONCENTRATIONS OF GELATIN

Concn. of gelatin %	*Drop time (t)* *sec*	*Rate of flow of mercury (m)* *mg/sec*	$m^{2/3}t^{1/6}$	*Diffusion current (i_d)* *µA*	*Diffusion current const. (I)*
0.001	4.80	1.76	1.89	6.28	3.32
0.002	4.73	1.74	1.86	6.22	3.34
0.005	4.73	1.76	1.87	6.28	3.36
0.01	4.50	1.76	1.86	6.18	3.33
0.02	4.35	1.77	1.87	6.18	3.31
0.05	4.35	1.76	1.86	5.97	3.21
0.1	4.34	1.74	1.84	5.88	3.20
0.2	4.33	1.77	1.87	5.71	3.05
0.4	4.33	1.74	1.84	5.31	2.88

TABLE V

DIFFUSION CURRENT CONSTANTS OF REDUCIBLE IONS IN THE SOLUTION CONTAINING VARIOUS CONCENTRATIONS OF GELATIN

Concn. of gelatin %	*Diffusion current constant*					
	Tl(I)[a]	*Pb(II)*[a]	*Pb acetate*[b]	*Cd(II)*[a]	*Zn(II)*[a]	*Co(II)*[a]
0.001	2.67	3.56	2.88	3.32	3.33	3.46
0.002	2.67	3.60	—	3.34	3.35	3.49
0.005	2.69	3.63	—	3.36	3.37	3.46
0.01	2.68	3.43	2.83	3.33	3.38	3.50
0.02	2.70	3.50	—	3.31	3.37	3.40
0.05	2.66	3.45	—	3.21	3.31	3.34
0.1	2.66	3.14	2.85	3.20	3.28	3.27
0.2	2.66	2.92	2.85	3.05	3.14	3.13
0.4	2.63	—	2.82	2.88	3.00	3.01

[a] In 0.1M potassium nitrate solution.
[b] In acetate buffer solution of pH 4.9.

TABLE VI

DIFFUSION CURRENT CONSTANTS OF REDUCIBLE IONS IN 0.1 M POTASSIUM NITRATE SOLUTIONS CONTAINING VARIOUS CONCENTRATIONS OF LEO

Concn. of LEO M	*Diffusion current constant*				
	Tl(I)	*Pb(II)*	*Cd(II)*	*Zn(II)*	*Co(II)*
$2 \cdot 10^{-6}$	2.64	3.63	3.34	3.35	3.38
$5 \cdot 10^{-6}$	2.65	3.59	3.31	3.36	3.35
$1 \cdot 10^{-5}$	2.64	3.59	3.33	3.40	3.44
$2 \cdot 10^{-5}$	2.66	3.59	3.39	3.45	3.49
$5 \cdot 10^{-5}$	2.68	3.64	3.38	a	a
$1 \cdot 10^{-4}$	2.70	3.61	3.36	a	a
$2 \cdot 10^{-4}$	2.69	3.62	3.35	a	a
$5 \cdot 10^{-4}$	2.69	3.61	3.39	a	a
$1 \cdot 10^{-3}$	2.65	3.67	3.39	a	a
Mean value	2.67 $\pm .02_3$	3.62 $\pm .02_7$	3.36 $\pm .03_0$	3.39 $\pm .04_6$	3.41 $\pm .06_2$

[a] Can not be determined accurately because of the hydrogen wave.

TABLE VII

RELATION OF THE DIFFUSION CURRENT CONSTANT, I, AND THE RELATIVE VISCOSITY, η_r, OF 0.1 M POTASSIUM NITRATE SOLUTION CONTAINING VARIOUS CONCENTRATIONS OF GELATIN

Concn. of gelatin %	*Relative viscosity (η_r)*	$I \cdot \eta_r^{1/2}$		
		Pb(II)	*Cd(II)*	*Zn(II)*
0.001	1.002	3.56	3.32	3.33
0.02	1.010	3.52	3.33	3.39
0.05	1.022	3.49	3.24	3.34
0.1	1.047	3.21	3.28	3.36
0.2	1.090	3.05	3.19	3.28
0.4	1.188	—	3.14	3.27

diffusion of simple electrolytes[15]. In fact, the decrease of diffusion current constants with the increase of the concentration of gelatin can not be explained by the effect of viscosity of the solution (Table VII). It is plausible, therefore, that the effect of gelatin on the diffusion current constant is due to the interaction of reducible ions with gelatin molecules. Previous papers[3,6] indicate that the effect of gelatin on the diffusion current of lead ion becomes pronounced when the pH of the solution is larger than 4. In neutral solutions, imidazol and carboxyl groups of a gelatin molecule are dissociated and many metal ions are supposed to be chemically combined with these active groups. Furthermore, there is a possibility that electroactive species are physically adsorbed on macro-molecules such as gelatin[6]. These interactions between electroactive species and gelatin molecules clearly reduce the concentration of free electroactive species in the solution, and, thus, decrease their diffusion current constants. The effect of gelatin on the diffusion current constant of thallium(I) ion was shown to be negligible in comparison with that on lead(II), cadmium(II) and cobalt(II) ions (Table V), which is in agreement with the well-known fact that the tendency of thallium(I) ion to make complex ions with complex-forming substances is usually very small. Table V also shows that the diffusion current constant of the lead acetate ion in the acetate buffer solution of pH 4.9 is kept approximately constant when the concentration of gelatin is increased. This might be explained by assuming that the presence of excess amounts of acetate ions, which easily react with lead ions to make lead acetate complex, prevents the relatively weak complex formation between lead(II) ions and gelatin molecules.

The discussion mentioned above is also confirmed by the experimental results of the effect of the concentration of lead(II) ions on the diffusion current in 0.1 M potassium nitrate solution containing 0.2% gelatin (Fig. 3). If the decrease of the diffusion current constant of the lead (II) ion is due to the increase of the viscosity of the solution, the ratio of the diffusion current to the concentration of the lead(II) ion, i_d/C, must remain constant independent of the concentration of the lead(II) ion. Fig. 3 clearly indicates that the value of i_d/C of the lead(II) ion gradually increases with the increase of the concentration of the lead(II) ion and reaches a constant value when the concentration of the lead(II) ion is higher than 1.5 mM. This can only be explained by assuming some kind of interaction between lead(II) ions and gelatin molecules.

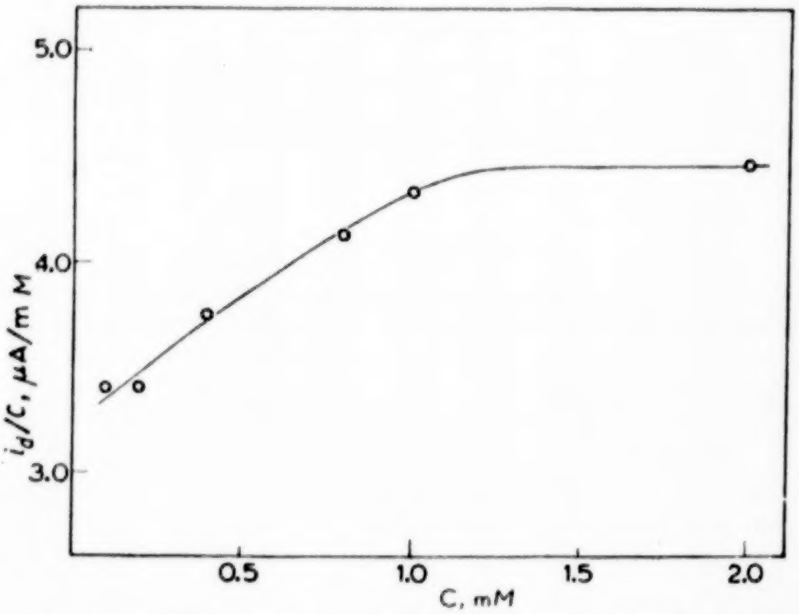

Fig. 3. Relation between i_d/C of Pb(II) ion and the bulk concentration of Pb(II) ion, C, in 0.1 M KNO$_3$ solution containing 0.2% gelatin.

In conclusion, it can be said that the addition of gelatin of relatively high concentration generally decreases diffusion current constants of many electroactive species because of the interaction between these electroactive species and gelatin molecules. In the polarographic analysis using a conventional DME, the concentration of gelatin as a maximum suppressor is usually less than 0.01%, where the effect of gelatin on the diffusion current constant is negligibly small. However, when the more sensitive methods, such as the use of the rotated dropping mercury electrode or the alternating current polarograph, are employed, this effect of gelatin will introduce some inevitable errors in the polarographic analysis.* By using LEO as a maximum suppressor instead of gelatin, a very good constancy of diffusion current constant is obtained in many cases. Furthermore, the solution of LEO is quite stable and completely free from deterioration. In these respects, the use of LEO as a maximum suppressor is much preferable to that of gelatin in the polarographic analysis.

ACKNOWLEDGEMENT

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SUMMARY

The effect of gelatin and LEO on diffusion current constants of some metal ions at the DME was investigated. LEO was shown to be very effective as a maximum suppressor, the MSP's of which were usually less than $1 \cdot 10^{-5} M$. Diffusion current constants were generally decreased by the addition of gelatin of relatively high concentration, mainly due to the interaction of electroactive species with gelatin molecules. It was found that diffusion current constants are unaffected by the addition of LEO over its wide concentration range. LEO has many advantages as a maximum suppressor, and the use of some kinds of synthetic detergents similar to LEO is strongly recommended in polarographic analysis of high sensitivity.

RÉSUMÉ

On a examiné l'influence de la gélatine et de l'éther polyoxyéthylènelaurylique sur les constantes du courant de diffusion de quelques ions métalliques, à l'électrode à goutte de mercure. L'emploi de l'éther polyoxyéthylènelaurylique présente des avantages et il est recommandé en polarographie.

ZUSAMMENFASSUNG

Es wurde der Einfluss von Gelatine und Lauryl-polyoxyäthylenäther auf die Konstanten der Diffusionsströme einiger Metallionen an der Quecksilbertropfelektrode untersucht. Lauryl-polyoxyäthylenäther verursacht keine Änderung der Konstanten und wird deshalb für polarographische Bestimmungen empfohlen.

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* The disadvantage of gelatin as a maximum suppressor in the polarographic analysis using a rotated dropping mercury electrode was recently pointed out by KOLTHOFF AND OKINAKA[4], when they recommended the use of polyacrylamide as a maximum suppressor.

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POTENTIOMETRIC STUDIES ON COPPER FERROCYANIDE

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Several research workers have investigated the reaction between copper salts and potassium ferrocyanide, mostly by analytical methods but also by physico-chemical methods; there is, however, hardly any agreement between the views expressed by these authors.

RAUTER[1] was of the opinion that copper ferrocyanide adsorbed some potassium ferrocyanide and that the precipitate, owing to this colloidal nature, was peptised before it could be washed entirely free of potassium ferrocyanide; hence purely analytical methods could not be of much use in determining the composition of copper ferrocyanide. WYROUBOFF[2] reported the formation of three compounds under varying conditions corresponding to the formulae: $Cu_2[Fe(CN)_6]$, $K_2Cu[Fe(CN)_6]$, and $K_2Cu[Fe(CN)_6]\cdot K_4Fe(CN)_6$. MULLER, WEGELIN AND KELLERHOFF[3] studied the compositions of the precipitates formed by the interaction of copper sulphate with $K_4Fe(CN)_6$ and also with hydroferrocyanic acid and expressed the view that a precipitate of constant composition can only be obtained when one of the components is in large excess. They suggested the formula $K_2Cu_3[Fe(CN)_6]_2$ for the compound that is brown in colour and $K_2Cu[Fe(CN)_6]$ for the yellow compound.

WILLIAMS[4] reported the formation of $Cu_4K_4[Fe(CN)_6]_3$ by precipitating solutions of $K_4Fe(CN)_6$ with a cupric salt, and of $Cu_6K_8[Fe(CN)_6]_5$ by the exact precipitation of $K_4Fe(CN)_6$ solutions containing a large excess of KCl. Compounds of variable compositions, such as $Cu_7K_6[Fe(CN)_6]_5\cdot 22H_2O$; $Cu_9K_2[Fe(CN)_6]_5\cdot 50H_2O$, are reported to have been formed under different conditions.

KOLTHOFF[5] titrated copper salts conductometrically with $K_4Fe(CN)_6$ and observed that the normal salt $Cu_2[Fe(CN)_6]$ was first precipitated. With more ferrocyanide this salt formed the double salt $K_2Cu_3[Fe(CN)_6]_2$, and this was followed by a third inflexion point corresponding to the formation of $K_4Cu_4[Fe(CN)_6]_3$. BRITTON AND DODD[6] could not confirm the results of KOLTHOFF but obtained two inflexion points corresponding to the formation of $Cu_2[Fe(CN)_6]\cdot x\ K_4Fe(CN)_6$ where $x = 0.16$ and 0.40. BHATTACHARYA AND GAUR[7] studied the composition by applying physico-chemical methods and suggested that the compound formed is $K_2Cu[Fe(CN)_6]$, which in excess of copper sulphate changes to $K_2Cu_3[Fe(CN)_6]_2$.

In view of the conflicting opinions and in the absence of any decisive views on the composition of copper ferrocyanide, it was considered worthwhile to make a more comprehensive study of its composition by applying electrometric methods, since these give more conclusive results regarding the composition of complex metallic ferro and ferricyanides (R. S. SAXENA *et al.*[8]). In this paper only the results of potentiometric titrations have been included and discussed.

EXPERIMENTAL

The $CuSO_4$ and $K_4Fe(CN)_6$ used were AnalaR (B.D.H.) chemicals. With various concentrations of the two salts in solution, potentiometric titrations were performed both by the direct and the reverse methods, *i.e.* by adding $K_4Fe(CN)_6$ solution from the micro-burette to the copper sulphate solution in the electrode cell and vice-versa. Potassium ferrocyanide solution containing 1% $K_3Fe(CN)_6$ was used to make the ferri–ferrocyanide electrode[9]. A bright platinum foil was dipped in the solution being titrated and used as an indicator electrode in conjunction with a saturated calomel electrode. The E.M.F. was measured on a Cambridge pH meter. The electrode cell was immersed in an electrically controlled thermostat to keep the temperature constant and the titration solution was stirred continuously by means of an electrically driven stirrer. The titrations were also carried out in the presence of alcohol and electrolytes such as NH_4NO_3, $(NH_4)_2SO_4$, K_2SO_4. Curves were plotted of the E(observed) *versus* the volume of the titrant added and from the sharp jump in potential shown on the titration curves, the equivalence point was found. This was further checked by calculating the maximum value of dE/dC in each case. 20 ml of the reagent was taken in the cell each time.

TABLE I

SUMMARY OF RESULTS OF POTENTIOMETRIC TITRATIONS

$K_4Fe(CN)_6$ solution molarity	$CuSO_4$ solution molarity	*Equivalence points* *ml of $K_4Fe(CN)_6$ or $CuSO_4$ required for the formation of $K_2Cu_3[Fe(CN)_6]_2$*					
		Calculated	*Found experimentally from dE/dC in presence of*				
			Alcohol		*NH_4NO_3 2 g*	*$(NH_4)_2SO_4$ 2 g*	*K_2SO_4 2 g*
			0%	*20%*			
		Direct titrations (Figs. 1–4)					
1/10	1/20	6.66	6.55	6.65	6.75	6.60	6.65
1/20	1/100	2.66	2.60	2.68	2.70	2.68	2.65
1/50	1/200	3.33	3.30	3.35	3.40	3.36	3.34
1/150	1/400	5.0	5.0	5.05	5.05	5.10	4.95
		Reverse titrations (Figs. 5–8)					
1/20	1/4	6.0	5.95	6.0	6.05	5.95	5.95
1/40	1/10	7.5	7.45	7.55	7.55	7.40	7.45
1/160	1/20	3.75	3.70	3.72	3.76	3.70	3.74
1/800	1/160	6.0	5.94	5.98	6.04	5.90	5.96

DISCUSSION

From the strengths of the solutions of $K_4Fe(CN)_6$ (M/10) and $CuSO_4$ (M/20), the calculated equivalents for the formation of further probable compounds are given below.

1. Titration values for 20 ml of M/20 $CuSO_4$ soln. in direct titration:

$K_2Cu[Fe(CN)_6]$;	$Cu_2[Fe(CN)_6]$;	$K_2Cu_3[Fe(CN)_6]_2$	$K_4Cu_4[Fe(CN)_6]_3$
10.0 ml	5.0 ml	6.66 ml	7.5 ml

(M/10 $K_4Fe(CN)_6$ solution)

2. Titration values for 20 ml of M/20 $K_4Fe(CN)_6$ solution in reverse titrations:

4.0 ml	8.0 ml	6.0 ml	5.33 ml

(M/4 $CuSO_4$ solution)

The titration values required for the formation of the above compounds, employing different concentrations of reactants, can be calculated accordingly both in the case of direct and reverse titrations.

The potential of the ferricyanide–ferrocyanide electrode at 25° is given by:

$$E = E_0 + 0.059 \log [\mathrm{Fe(CN)_6}]^{-3} / [\mathrm{Fe(CN)_6}]^{-4}.$$

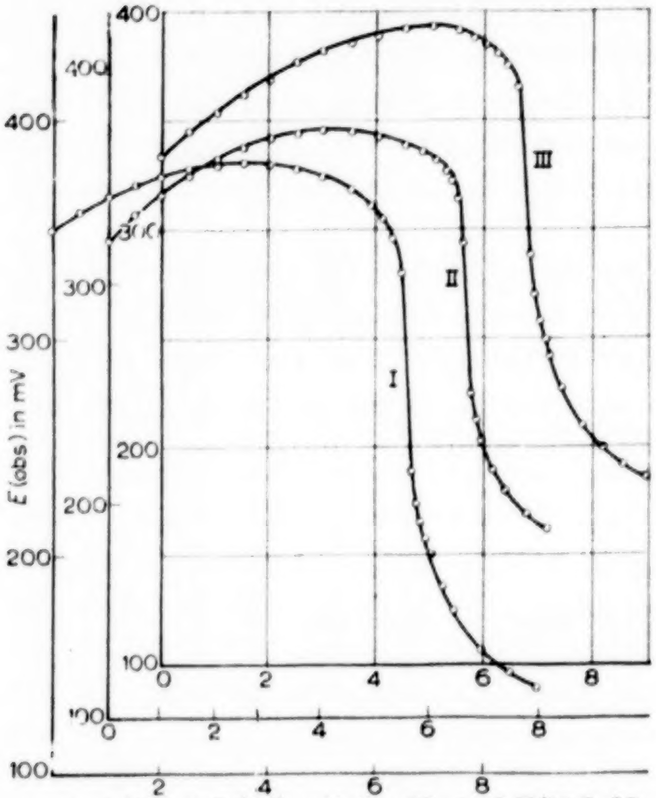

Fig. 1.

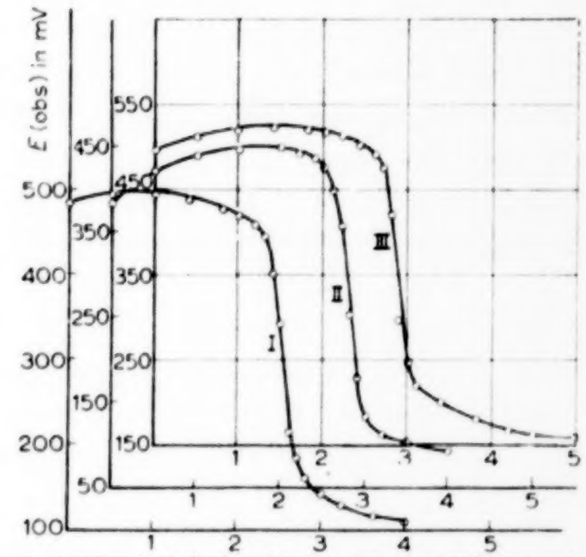

Fig. 2.

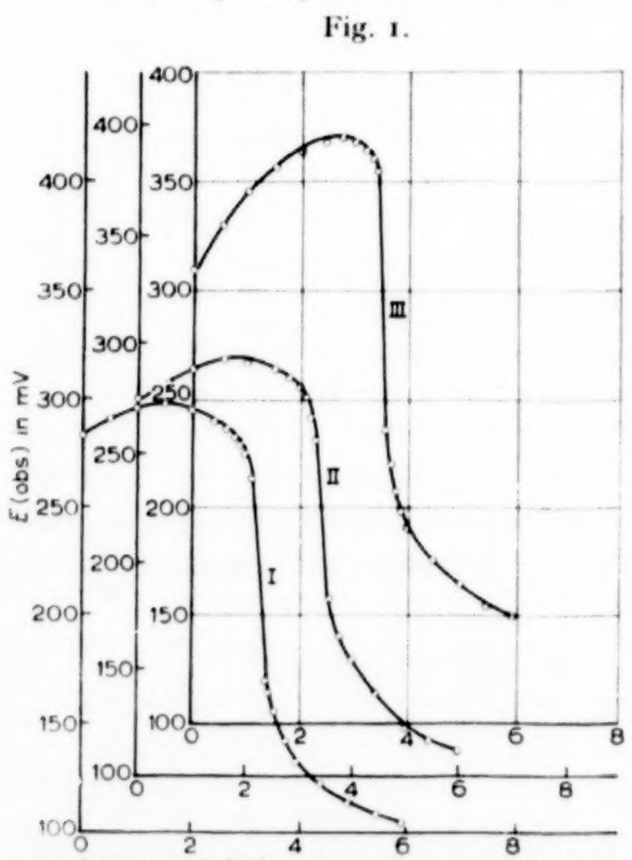

Fig. 3.

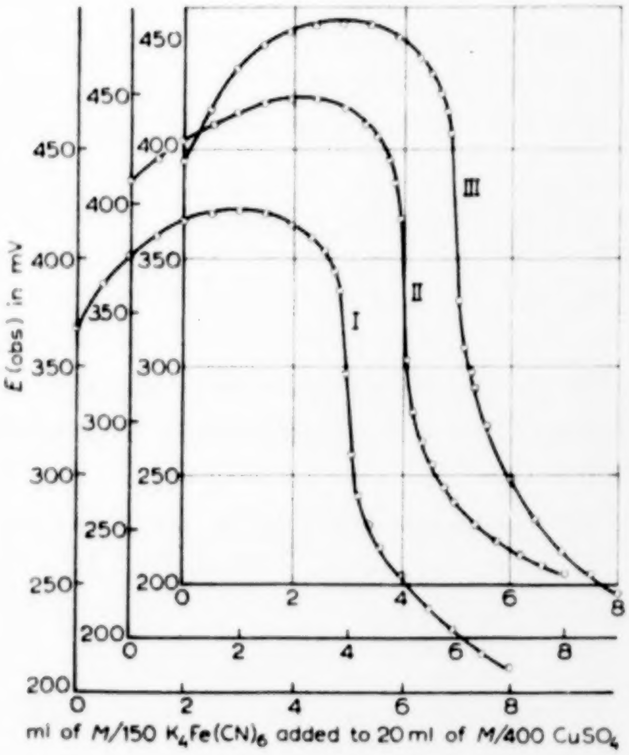

Fig. 4.

Figs. 1–4. Direct titrations. Curve I: 0% alcohol; curve II: 20% alcohol; curve III: 2 g NH_4NO_3.

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When copper sulphate solution is titrated with potassium ferrocyanide solution containing a little ferricyanide solution, the ferrocyanide is removed until all the metal is precipitated. As long as the ferrocyanide ions are removed, the potential remains in the oxidising region, but as the first excess of ferrocyanide is added, a sharp change in the E.M.F. of the titration cell is observed at the equivalence point. In the reverse titrations (when $CuSO_4$ solution is added from the micro-burette to $K_4Fe(CN)_6$ in the cell) the ferrocyanide ions are removed from the solution by precipitation and the E.M.F. of the cell remains practically constant. But when the last traces of the ferrocyanide ions have been removed (*i.e.* in the vicinity of the end-point), a sharp upward jump in potential is observed indicating the end-point. The ferri–ferrocyanide electrode ceases to work after the equivalence point has been crossed and hence the E.M.F. assumes a practically constant value.

In the direct titration curves (Figs. 1–4), the E.M.F. at first slightly rises at the beginning of the reaction, then becomes practically constant and afterwards begins to decrease with a sharp fall in potential being observed at the end-point. In the reverse titrations (Figs. 5–8), however, the E.M.F. gradually increases from the start of the reaction, and a marked upward jump is obtained at the equivalence point after which the potential assumes a constant value. The potentiometric titration curves are regular in form.

It was observed that copper ferrocyanide, which is formed as a chocolate brown precipitate, is deposited on the platinum electrode, making it less sensitive. Under these conditions the results are irregular, it takes a long time for the potential to become constant and the titration curves are peculiar in shape. Hence care must be taken that the electrode is not entirely covered with the precipitate. Is is necessary that the platinum electrode should be cleaned with nitric acid after each titration, followed by rubbing with emery paper and igniting. Continuous stirring in the neighbourhood of the electrode has a favourable effect. The sharpness of the potential break and the accuracy of the end-point are dependent upon these precautions.

It is clear from Figs. 1–8 and the summary of results given in Table I that the reaction between $CuSO_4$ and $K_4Fe(CN)_6$ can be successfully followed potentiometrically using a ferri–ferrocyanide electrode, with either of the reactants used as the titrant. The point of equivalence obtained from the maximum dE/dC and from the sharp inflexion in the curves, occurs at a stage where the molecular ratio of the reactants $K_4Fe(CN)_6$ and $CuSO_4$ is 2:3 corresponding to the formation of $K_2Cu_3[(Fe(CN)_6]_2$, and is very different from those required for the formation of other probable compounds $K_2Cu[Fe(CN)_6]$, $Cu_2[Fe(CN)_6]$, $K_4Cu_4[Fe(CN)_6]_3$ etc., as reported earlier in the literature. The curves have a regular form, a marked break in potential is observed at the end-point and the results are accurate and reproducible. In the presence of alcohol, no particular change in the nature of the curves or in the magnitude of the break in potential is obtained, except that the observed end-point is slightly nearer the calculated value (see Table I). This may be due to the decrease in solubility of copper ferrocyanide and also to suppression of the adsorption of the reacting ions by the precipitate in presence of alcohol. The addition of electrolytes such as NH_4NO_3, $(NH_4)_2SO_4$ and K_2SO_4, has practically no effect on the accuracy of the end-point and the nature of the curves but the magnitude of the break in potential increases when they are present.

Potentiometric titrations yield very accurate and reproducible results and afford a fairly good method for the quantitative determination of copper solutions. The titration is simple, rapid and accurate. The composition of copper ferrocyanide calculated from E.M.F. measurements is best represented by the molecular formula $K_2Cu_3[Fe(CN)_6]_2$.

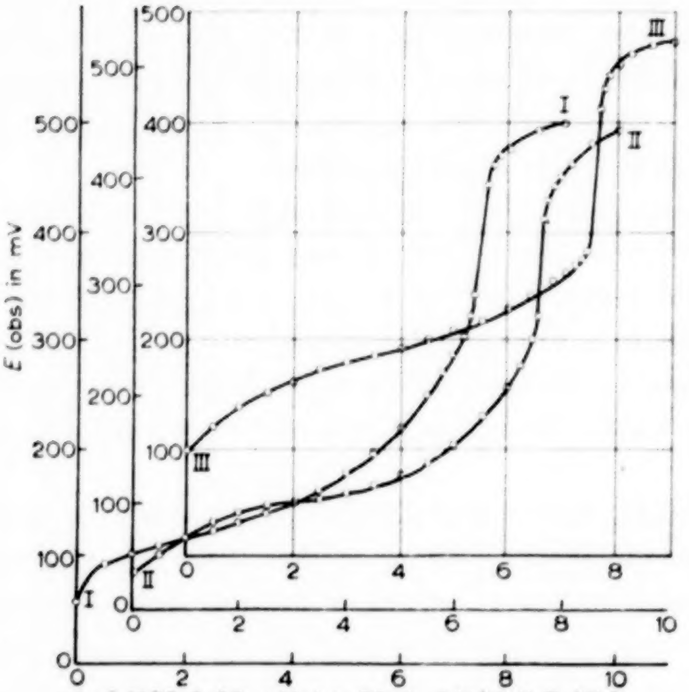

Fig. 5.

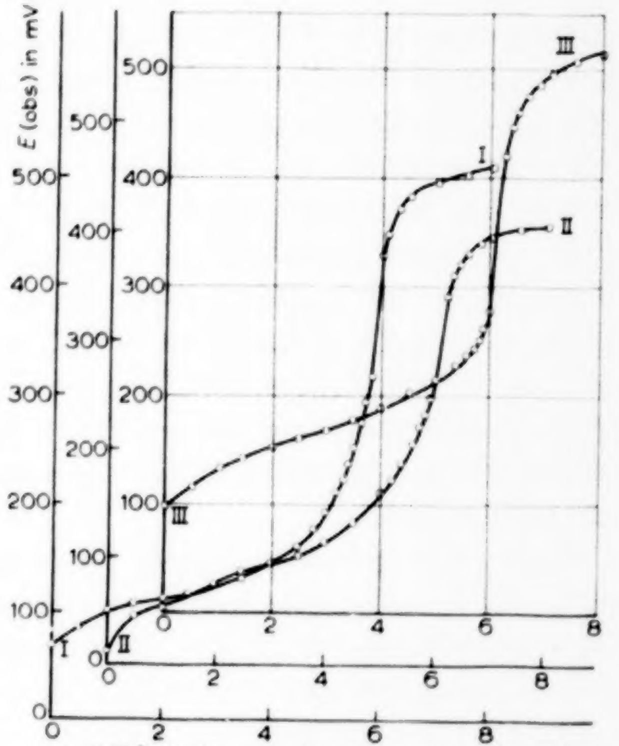

Fig. 6.

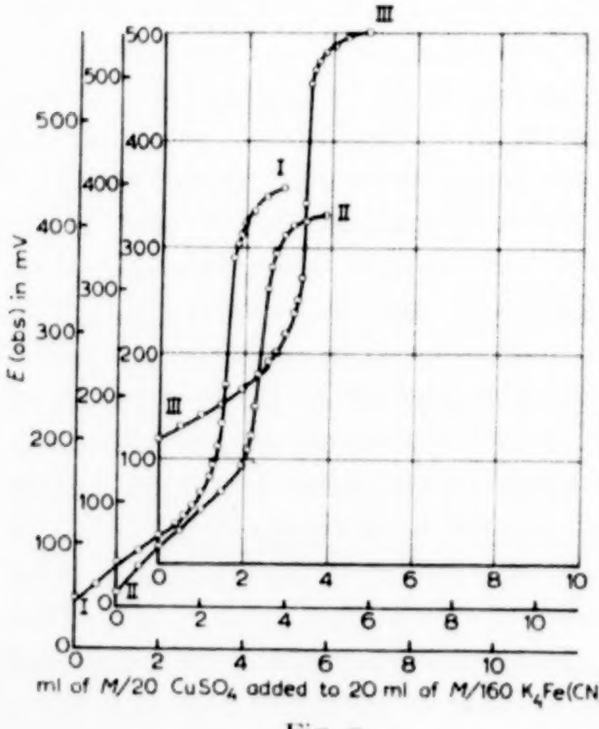

Fig. 7.

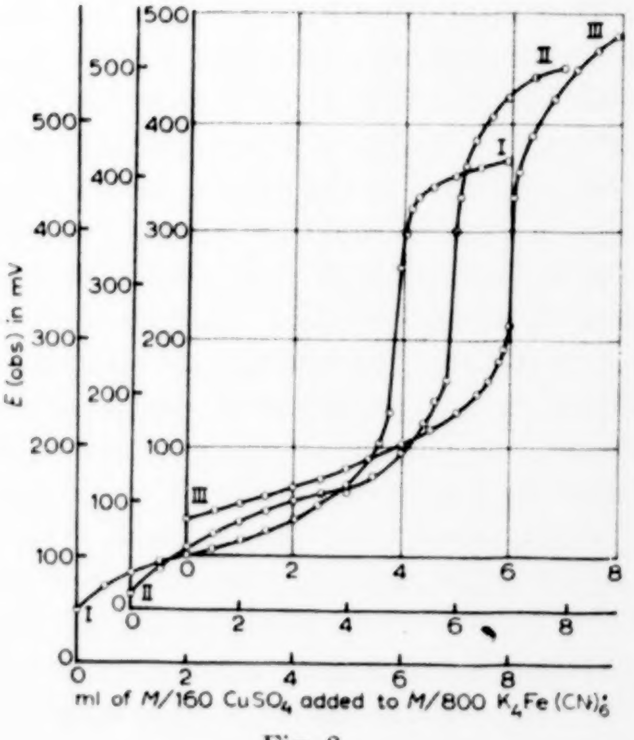

Fig. 8.

Figs. 5–8. Inverse titrations. Curve I: 0% alcohol; curve II: 20% alcohol; curve III: 2 g NH_4NO_3.

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SUMMARY

The formation and precipitation of copper ferrocyanide has been studied by potentiometric titrations of $CuSO_4$ and $K_4Fe(CN)_6$ at various concentrations using a ferricyanide–ferrocyanide electrode; each of the reactants was alternately used as the titrant. The end-point obtained from the maximum value of dE/dC corresponds to the formation of a compound with the molecular formula $K_2Cu_3[Fe(CN)_6]_2$. The titration curves have a regular form, a sharp break in potential occurs at the end-point and the results are accurate and reproducible. The method is simple and rapid and offers a fairly accurate means of determining copper in solutions. The effects of ethanol and electrolytes such as NH_4NO_3, $(NH_4)_2SO_4$ and K_2SO_4 on the end-point as well as on the nature of the curves were investigated.

RÉSUMÉ

La précipitation du ferrocyanure de cuivre a été étudiée par potentiométrie. On peut admettre la formation du composé $K_2Cu_3[Fe(CN)_6]_2$. Cette méthode simple et rapide permet le dosage du cuivre.

ZUSAMMENFASSUNG

Der Verlauf der Niederschlagsbildung von Kupferferrocyanid wurde potentiometrisch verfolgt. Beim Endpunkt der Titration entspricht die Zusammensetzung des Niederschlages der Formel $K_2Cu_3[Fe(CN)_6]_2$. Die Methode erlaubt eine einfache und rasche Kupferbestimmung.

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BUCHBESPRECHUNG

Analyse der Fette und Fettprodukte einschl. der Wachse, Harze und verwandter Stoffe, herausgegeben von H. P. Kaufmann, unter Mitwirkung namhafter Fachleute in 2 Bänden mit zus. 1860 S., Springer Verlag Berlin, Göttingen, Heidelberg, 1958, preis (beide Bände): DM 248.—.

Der erste Band (allgemeiner Teil) behandelt auf *ca.* 1100 Seiten die Chemie und Analyse der reinen Fette, deren Bausteine und Begleitstoffe (Sterine, Lipochrome, Phosphatide usw.) sowie die natürlichen Wachse und Harze als verwandte Stoffe. Die Zerlegung von Fettsäuregemischen und die Bestimmung der Einzelbestandteile wird sehr ausführlich beschrieben, wobei den physikalischen Methoden sehr viel Platz eingeräumt wird. Es braucht wohl nicht besonders hervorgehoben zu werden, dass alle modernen Methoden der Analyse und Trennung (z.B. mikro- und chromatographische Methoden) die ihnen gebührende Berücksichtigung erfahren haben.

Der zweite Band (spezieller Teil, *ca.* 650 Seiten) beschreibt die mikroskopische Untersuchung der fettliefernden Rohstoffe, die Analyse der Nahrungsfette, Milcherzeugnisse und Kakaofette einschliesslich der Methoden zur Bestimmung der Verdorbenheit von Fetten. Der grössere Teil dieses Bandes befasst sich mit den Untersuchungsmethoden der technisch wichtigen Fette, Fettprodukte und verwandten Stoffen (Textil-Öle, Seifen, wasch-aktive Stoffe, sulfonierte Öle und Fette, Anstrichmittel, Faktis, Lederfettungsmittel, Wollfett, Glycerin und andere Polyalkohole).

Dieses Werk, aus der Hand des sehr bekannten Fachmannes unter Mitarbeit zahlreicher anderer Fachleute, füllt zweifellos eine lang empfundene Lücke in der chemischen Fachliteratur aus. Wer

sich mit der Untersuchung von Fettprodukten, besonders auf dem technischen Sektor, zu befassen hat, wird das Erscheinen dieses ausgezeichneten Buches sehr begrüssen. Durch die Beschreibung der Trennungs- und Analysenmethoden für kleinste Substanzmengen wird aber auch der auf biologischem oder physiologischem Gebiet arbeitende Wissenschaftler das Werk als unentbehrlich betrachten. Bei den technischen Produkten sind, ihrer Bedeutung entsprechend, die Analysenmethoden für synthetische Waschmittel und Anstrichstoffe sehr ausführlich behandelt. Die Analytik der Anstrichmittel umfasst u.a. Nachweis- und Bestimmungsmethoden der einzelnen Kunstharze, wodurch dieses Kapitel auch für die Untersuchung von Kunststoffen wertvolle Hinweise gibt. Der Titel des Werkes ist vielleicht etwas irreführend, da man vermuten könnte, es handle sich um eine Sammlung von Analysenvorschriften für Fette und verwandte Produkte. In Wirklichkeit ist der Charakter des Werkes mehr der eines Handbuches der Fettchemie und verwandter Gebiete, denn auch der Wissenschaftler, der sich mit Fragen der Synthese, Strukturermittlung und anderen Problemen dieser Körperklasse abgibt, die mit der Analyse direkt nichts zu tun haben, wird mit Vorteil dieses Werk zu Rate ziehen.

K. EDER (Genève)

Announcement

CHROMATOGRAPHIE DES GAZ — GROUPE DE STANDARDISATION

Sous l'égide de la section de Chimie Analytique de l'Union Internationale de Chimie Pure et Appliquée, un groupe a été constitué en vue de présenter au Conseil de l'Union des propositions concernant la *standardisation de la nomenclature et de la présentation des données de Chromatographie des gaz.*

Ce groupe est présidé par Mr. D. AMBROSE (National Chemical Laboratory, Teddington, G.B.). Il comprend Messieurs: Dr. A. T. JAMES (Grande Bretagne), Prof. Dr. A. I. M. KEULEMANS (Pays-Bas), Dr. E. KOVATS (Suisse), Dr. R. RÖCK (Allemagne), Dr. F. H. STROSS (U.S.A.) et C. ROUIT, Ing. Dr. (France).

Le travail actuel du groupe consiste à mettre au point un document basé sur deux articles parus dans *Anal. Chem.*, 30, Nr. 10 (octobre 1958) 1582: Presentation of Gas-Liquid Chromatographic Retention Data, par D. AMBROSE, A. I. M. KEULEMANS ET J. H. PURNELL.

Anal. Chem. 30, Nr. 10 (octobre 1958) 1586: Terms and units in gas chromatography, par H. W. JOHNSON ET F. H. STROSS.

En vue de rendre aussi ouverte et aussi large que possible la discussion qui conduira à la publication du document envisagé, toutes les personnes qui utilisent la chromatographie des gaz ou travaillent à en développer les théories et les applications sont invitées à collaborer avec le groupe.

A cet effet, leurs remarques, critiques, suggestions ou approbations concernant les données des publications sous référence pourraient être adressées à:

Monsieur CHARLES ROUIT, Chef du Département Laboratoires, Raffinerie de la Société Française des Pétroles BP, Lavéra-Martigues (Bouches-du-Rhône).

L'étape initiale conduira à un document en anglais. Un document identique en français est en préparation et sera proposé en temps utile pour discussion aux intéressés.

TURBIDIMETRIC TITRATIONS*

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Turbidimetric measurements can be used in two general ways in analytical chemistry. In one method, the unknown component is put into suspension by precipitation with an appropriate reagent, and the turbidity of the suspension is compared by one of several possible techniques with that of one or more standard suspensions. In the other method, a solution of the unknown is titrated by a solution of a precipitating agent, and the end-point is obtained by means of a plot of measured turbidity *vs.* volume of added reagent.

One chief limiting factor in all analytical turbidimetric procedures has been the irreproducibility of the physical form of the precipitate. This factor is more serious when comparison must be made with standards than in titrations, because it is not possible to precipitate the unknown and the standards under identical conditions. Extensive experimentation in this laboratory has revealed that the physical form of a precipitate is determined largely by the first batch of precipitated particles, even though there is considerable random variation among a series of initial batches of precipitate in supposedly identical trials. It seems, therefore, that titration procedures should be distinctly superior to those turbidimetric procedures which are based upon comparisons with standards. The turbidimetric method of detecting titration end-points with precipitation reactions is of particular interest because no general type chemical indicators have been developed for precipitation titrations as has been done for neutralization and oxidation–reduction titrations.

Several specific applications of turbidimetric titrations have been reported in the literature, including those in a number of papers by BOBTELSKY *et al.*[1-3], and others. It is the purpose of the present study to examine the roles of nucleation and crystal growth in the precipitation reaction by the preparation of calculated titration curves and, from these curves, to make and to test certain predictions concerning turbidimetric titrations.

CALCULATED TITRATION CURVES

The first portion of precipitating agent forms the first batch of particles by both nucleation and crystal growth. This growth may be designated "initial growth." It is conceivable that the next equal increment of mass of precipitate could form in one of four ways: (A) it could consist of further nucleation and initial growth just as did the first increment; (B) it could consist of uniform growth on all crystal faces of the particles already present; (C) it could consist of preferential growth on certain crystal face(s) of the precipitate already present; (D) it could consist of some new nucleation

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* Contribution 871, Chemistry department, Indiana University. Work supported by the U.S. Atomic Energy Commission under Contract AT(11-1)-497.

but primarily of further growth. Situation (D) is intermediate between situations (A) and either (B) or (C). Calculated curves of total surface area *vs.* mass of precipitate are shown in Fig. 1 for situations (A) and (B); the area and the mass of the initial batch of particles are both assigned the arbitrary values of 0.1. The curve for situation (B) applies whatever the particle shape is, *i.e.*, whether spheres, cubes, etc. Curves calculated for situation (C) lie intermediate between (A) and (B), with the exact placement relative to (A) and (B) determined by the particle shape and by which face(s) bear the additional growth. Situation (D) is also an intermediate one, so the two curves of Fig. 1 are the extremes with all other possibilities lying between.

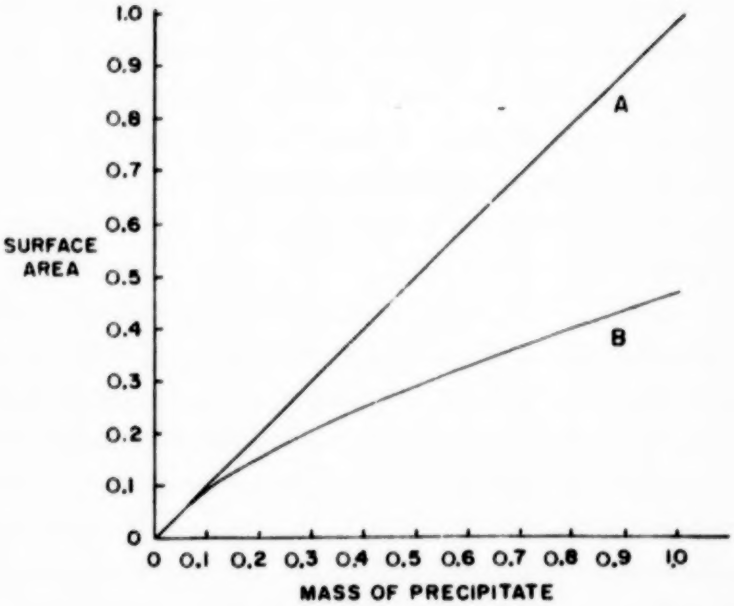

Fig. 1. Calculated curves for conditions of (A) continual new nucleation and initial growth with each increment of mass of precipitate and (B) crystal growth only beyond first increment of mass of precipitate (both axes in arbitrary units).

It is now necessary to relate the curves of Fig. 1 to titration curves. By analogy to the Lambert-Beer law for light-absorbing systems, it can be expected that the "apparent optical density" (log of the ratio of intensity of incident light to intensity of transmitted light) of a light-scattering system should be a linear function of the total surface area of the suspended particles. This expectation was verified experimentally by measurements upon aqueous suspensions of known, but varied, numbers of uniform-sized spheres of a polystyrene latex. Furthermore, the mass of precipitate present in a turbidimetric titration is a linear function of the volume of added reagent, assuming only that the precipitate has a negligible solubility. Therefore, the plots of Fig. 1 are in fact calculated titration curves of optical density *vs.* volume of added titrant, both in arbitrary units, up to the equivalence point. Beyond the equivalence point, no further precipitate is formed, so the titration curve should be a horizontal line from this point on. Thus each end-point is marked by the transition from a rising to a constant optical density. For situation (A) there is a linear increase in optical density up to the equivalence point, while situation (B) is marked both by curvature and by a lower optical density. Selective growth without further nucleation, situation (C) is characterized by a titration curve between (A) and (B), and situation (D) is also an intermediate one.

There are several reasons why actual titrations curves may be expected to differ from the calculated ones. First, a precipitate tends to recrystallize, coagulate and settle, at a rate which is neither constant nor uniformly varying throughout the titration. This factor tends to decrease the optical density, to make the end-point transition less distinct, and if the precipitate settles below the level at which the light beam traverses the sample to make it impossible to obtain meaningful measurements of optical density. Second, as the titration proceeds toward the equivalence point, the tendency to nucleate may be expected to decrease gradually and the corresponding tendency toward crystal growth to increase. This factor consists of a gradual shift from situation (A) to situation (B) during the titration, so also renders less distinct the transition from a rising to a constant optical density. Third, the precipitates are never completely insoluble, and the solubility is generally greatest right at the equivalence point when neither ion is present in excess. This factor also tends to make the end-point "break" on the titration curve less distinct. Fourth, some scatter of points may be expected from random, unknown and/or uncontrolled, factors, even though the randomness is much less in titrations than when turbidities must be compared to standards.

Several predictions can be made on the basis of the considerations thus far, including the following:

a. Any experimental factor which enhances continual nucleation at the expense of further crystal growth should be desirable, because the end-point transition from a rising to a constant optical density is most distinct in situation (A).

b. Any experimental factor which tends to minimize coagulation and settling of the precipitate should render the end-points more distinct.

c. Any experimental factor increasing the extent of initial nucleation should increase the optical density and make titrations of lower concentrations of unknown possible.

d. Any experimental factor exerting considerable control over the nucleation-growth phenomena should make less significant those random factors which cause scatter of points on the titration curve.

EFFECTS OF NON-IONIC DETERGENTS

It has been found that, in some instances, the presence of a small amount of a non-ionic detergent in the titrated solution, serves as an experimental factor which fulfills to an appreciable extent all four of the desiderata of the preceding paragraph. Possibly the detergent molecules are adsorbed upon the surfaces of the particles of precipitate in such a way as to prevent or to minimize further growth of those particles.

Many measurements have been made on numerous systems. The action of the non-ionic detergents is quite selective, being quite pronounced with some precipitation reactions and of no significance whatever in others. For each system, titrations were performed without and with each of several added agents, and other experimental factors were varied as seemed desirable. The optical density, as measured on a Bausch and Lomb Spectronic Colorimeter or a Coleman Nefluorophotometer, was plotted *vs.* volume of added titrant, and the plots were examined for such factors as scatter of points from a smooth curve, magnitude of optical density, linearity prior to end-point, whether strictly horizontal beyond end-point or not, sharpness of transition from rising to constant optical density, and agreement between observed and known end-points.

Precipitation of barium sulfate

Two non-ionic detergents, Tergitol and Triton, were found to influence the precipitation process quite markedly. They increased the optical density considerably, speeded up the precipitation reaction so that a constant reading was reached more quickly after each increment of titrant, and minimized the tendency for the precipitate to coagulate and to settle to the bottom of the vessel. However, the titration curves are sufficiently rounded at and near the equivalence points, even with the surfactants present, to make accurate recognition of end-points difficult.

Precipitation of lead chromate

The non-ionic detergents exerted practically no influence on the nucleation-growth characteristics of lead chromate.

Precipitation of lead molybdate

The non-ionic surfactants failed to influence the precipitation process. However, another addition agent, dextrin, did enhance nucleation, as evidenced by an increased optical density, and it also prevented coagulation of the precipitate.

Precipitation of lead carbonate

In the titration of lead nitrate by sodium carbonate, the effects of non-ionic detergents were quite pronounced. The agents served to increase the optical density, to minimize settling of the precipitate during the titration, and to make the end-point transition from a rising optical density to a constant one somewhat sharper and more distinct. In this system, as in some others, the end-point is more distinct with more concentrated reagents than with extremely dilute ones, but the total optical density is difficult to measure accurately if it becomes too high.

Precipitation of calcium oxalate

In some titrations of calcium ion by oxalate ion, the presence of non-ionic surfactants, either Tergitol or Triton, served to result in higher optical densities, thereby making determinations of quite low concentration of calcium possible. However, the effect is not consistently reproducible, for the agents exerted no influence in many experiments. Other random variables, such as rate of mixing and size of increment of titrant, are much more significant. The agents do minimize coagulation, but this is not a serious problem in this determination anyway.

Precipitation of silver chloride

Both non-ionic surfactants, Tergitol and Triton, caused a slight decrease in optical density, perhaps due to a slightly enhanced coagulation rather than to actual increase in crystal growth, but the agents did not influence the accuracy or the precision of this turbidimetric titration determination. Gelatin, a common dispersing agent, made the end-point transition completely non-recognizable. Dextrin had negligible influence.

Precipitation of nickel dimethylglyoxime

Triton or Tergitol, particularly when gelatin was also present, resulted in reasonably good titration curves. Without any addition agents, the random scatter on the titration curves was considerable. It was observed that the precipitate of nickel dimethylglyoxime tended to stick to the glass walls and to float to the surface when no surfactant was present, but that the suspension was made much more stable and uniform in the presence of the addition agents.

Precipitation of calcium fluoride

A turbidimetric titration procedure involving the precipitation of calcium fluoride has recently been published[4]. It was found in the present study that both Tergitol and Triton cause an increase in optical density of the suspended precipitate, thus signifying enhanced nucleation at the expense of crystal growth. The agents also made the titration curves more linear prior to the end-points, and the accuracy of the determination was improved appreciably.

SUMMARY

The physical form of a precipitate is subject to considerable random variation but is determined largely by the first batch of precipitated particles. So turbidimetric titration procedures are generally preferable to turbidimetric determinations based upon comparisons to standards. Titration curves of optical density *vs.* volume of titrant have been calculated for various conditions of nucleation and crystal growth. It is predicted from the calculated curves that any factor which enhances nucleation at the expense of crystal growth should improve the analytical usefulness of turbidimetric titrations. One such factor is the presence of a non-ionic surfactant which is apparently adsorbed on crystal surfaces, thereby minimizing further crystal growth. The prediction is verified with some precipitation reactions, but the surfactant is of no effect on others.

RÉSUMÉ

Les méthodes de titrage turbidimétrique (consistant à mesurer la densité optique en fonction du volume de réactif) se montrent généralement préférables aux dosages par comparaison avec des étalons. Des courbes de titrage ont été calculées dans diverses conditions.

ZUSAMMENFASSUNG

Turbidimetrische Titrationen (Messung der optischen Dichte als Funktion der Menge zugesetzter Reagenzlösung) sind im allgemeinen den Vergleichsmethoden mit einer Standard-Trübung überlegen. Die Änderung der optischen Dichte in Abhängigkeit von der Menge Reagenzlösung unter verschiedenen Bedingungen wurde errechnet und in Kurven dargestellt.

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DETERMINATION OF STRONG ACID MIXTURES

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The recently proposed tetraalkylammonium hydroxides[1-4] are gaining wide acceptance as titrants for the determination of acidic compounds and acid mixtures because their use supplants a large number of other diverse titrimetric methods. Among the applications recommended for these quaternary ammonium hydroxides are several procedures for differentiating titrations of both weak and strong acids[3,5,6]. None of these offer supporting data for quantitative analysis of mixtures containing strong acids.

The authors have proposed an improved quaternary ammonium hydroxide titrant for the determination of strong acids[7] and in another report discussed solvent-solute reactions which occur in the titration of strong acids in a number of nonaqueous solvents[8]. These studies provided the basis for the exact quantitative determination of acid mixtures containing strong acids. In this work, differentiating titrations of several acid mixtures are described with supporting quantitative data. Although emphasis is placed on mixtures containing sulfuric acid, the analysis of other acid mixtures is outlined to illustrate the potential of this procedure, and to demonstrate further the exceeding versatility of quaternary ammonium hydroxide titrants.

PROCEDURE

The apparatus and preparation of reagents were described previously[7].

Dissolve 0.7–0.9 mequivs. of total acid in 50 ml of pyridine and titrate potentiometrically with 0.1*N* tetrabutylammonium hydroxide under a nitrogen atmosphere. Determine the end-points from a plot of potential *vs.* volume of titrant. Correct the final end-point for the solvent blank. When two or more inflections are present in the curve, use the difference between successive end-points to calculate the volume of titrant equivalent to the acids represented.

If any of the acids are pyridine insoluble, dissolve in 1.5 ml water prior to adding the pyridine. The addition of three drops of azo-violet indicator solution is often beneficial in the discernment of one or more of the end-points.

EXPERIMENTAL

Titration of strong acid mixtures

Fig. 1 typifies the potentiometric curve obtained when titrating a mixture of sulfuric acid and another monobasic strong acid. In this curve the first inflection includes the neutralization of nitric acid and the first equivalent of sulfuric acid, the second inflection represents the neutralization of the second equivalent of sulfuric

TABLE I

ANALYSIS OF NITRIC–SULFURIC ACID MIXTURES

Nitric acid			*Sulfuric acid*		
Added mg	*Found* mg	*Recovery* %	*Added* mg	*Found* mg	*Recovery* %
42.58	42.64	100.1	16.13	16.13	100.0
8.52	8.53	100.1	32.26	32.16	99.7
53.23	53.14	99.8	9.68	9.70	100.2
12.77	12.79	100.2	25.81	25.73	99.7
42.58	42.58	100.0	6.45	6.43	99.7

acid. Table I shows data on the analysis of known mixtures of sulfuric and nitric acids.

Titration of sulfuric–phosphoric acid mixtures yielded a potentiometric curve with three inflections, the first representing the neutralization of the first equivalent of sulfuric acid, the second representing the neutralization of the second sulfuric and first phosphoric acid equivalents, and the third representing the neutralization of the second phosphoric acid equivalent. The third phosphoric acid equivalent does not titrate in this mixture. This curve is illustrated in Fig. 2.

Table II lists the results obtained in the analysis of sulfuric–phosphoric acid mixtures.

Mixtures of phosphoric acid with *p*-toluenesulfonic, nitric and hydrochloric acid, respectively, on titration yielded a potentiometric curve similar to that illustrated in Fig. 2. Three inflections were obtained, the first representing the neutralization of the *p*-toluenesulfonic, nitric or hydrochloric acid, the second and third representing

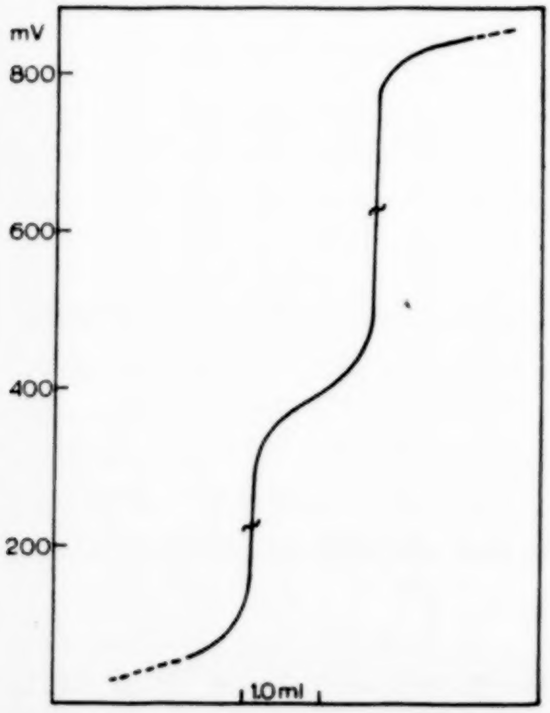

Fig. 1. Titration of nitric–sulfuric acid mixture.

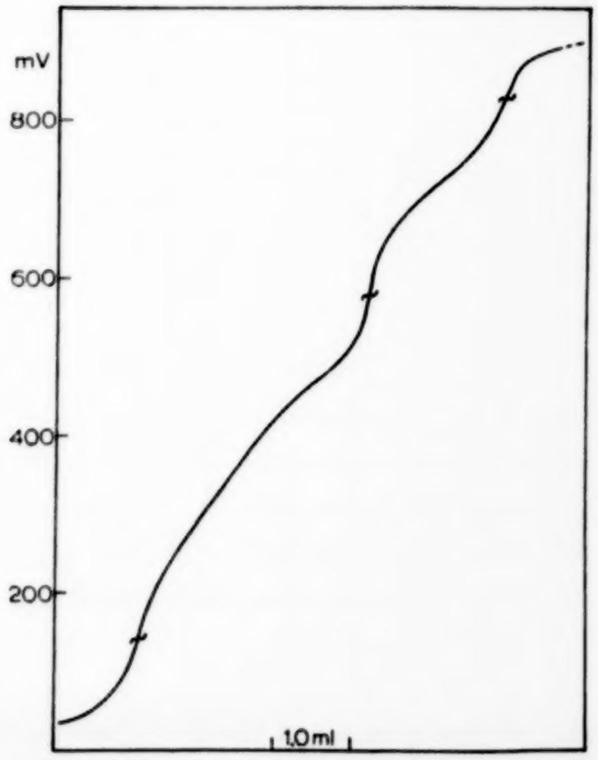

Fig. 2. Titration of phosphoric–sulfuric acid mixture.

TABLE II

ANALYSIS OF SULFURIC–PHOSPHORIC ACID MIXTURES

Phosphoric acid		Recovery %	*Sulfuric acid*		Recovery %
Added mg	*Found mg*		*Added mg*	*Found mg*	
17.94	17.84	99.4	11.02	10.91	99.0
29.15	28.95	99.3	15.20	15.30	100.7
35.87	36.08	100.6	22.03	22.03	100.0
18.24	18.24	100.0	25.09	25.09	100.0
17.94	17.94	100.0	25.09	24.99	99.6

TABLE III

ANALYSIS OF *p*-TOLUENESULFONIC–PHOSPHORIC ACID MIXTURES

p-Toluenesulfonic acid		Recovery %	*Phosphoric acid*		Recovery %
Added mg	*Found mg*		*Added mg*	*Found mg*	
50.94	50.94	100.0	28.48	28.58	100.4
84.90	85.07	100.2	14.24	14.14	99.3
135.84	134.41	98.9	22.78	22.79	100.0
33.96	34.14	100.5	42.72	42.52	99.5

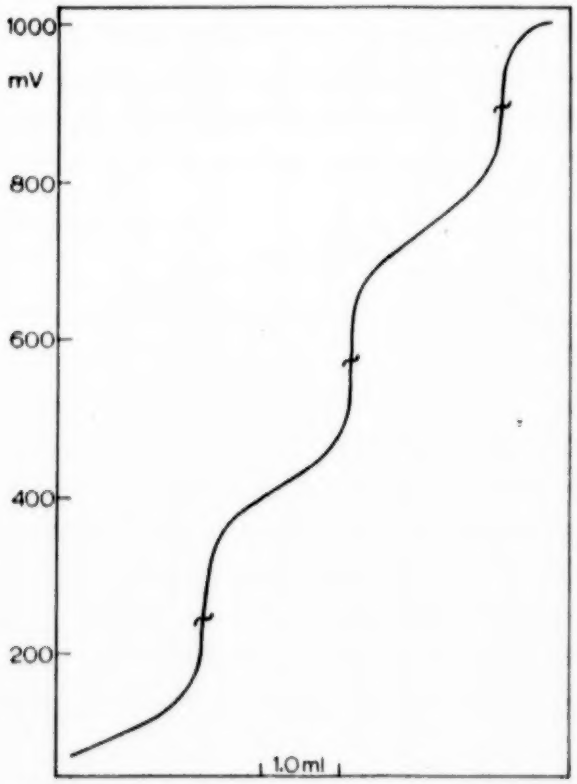

Fig. 3. Titration of *p*-toluenesulfonic acid, propionic acid and *p*-benzylphenol mixture.

the neutralization of the first two equivalents of phosphoric acid. Table III gives the results from analysis of *p*-toluenesulfonic-phosphoric acid mixtures.

Results for the analysis of several other strong acid mixtures are given in Table IV.

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The potentiometric curve for each of the mixtures containing sulfuric acid was similar to that illustrated in Fig. 1, the curves for the mixtures containing phosphoric acid were similar to that illustrated in Fig. 2.

TABLE IV

ANALYSIS OF STRONG ACID MIXTURES

Compounds	*Added* mg	*Found* mg	*Recovery* %
Perchloric acid	52.24	52.35	100.2
Sulfuric acid	25.86	25.96	100.4
Hydrochloric acid	16.76	16.76	100.0
Sulfuric acid	17.50	17.50	100.0
Benzenesulfonic acid	55.94	55.36	99.0
Sulfuric acid	25.96	26.06	100.4
3-Amino-*p*-toluenesulfonic acid	94.58	93.52	98.9
Sulfuric acid	25.96	26.16	100.8
Naphalene-β-sulfonic acid	53.07	52.60	99.1
Sulfuric acid	28.25	28.40	100.5
Sulfamic acid	57.17	57.37	100.4
Sulfuric acid	29.63	29.52	99.6
p-Toluenesulfonic acid	80.95	80.95	100.0
Sulfuric acid	25.91	25.86	99.8
Methanesulfonic acid	20.15	20.05	99.5
Sulfuric acid	25.86	25.86	100.0
Benzenesulfonyl chloride	71.68	72.05	100.5
Sulfuric acid	26.16	26.06	99.6
Nitric acid	25.90	25.84	99.8
Phosphoric acid	28.48	28.48	100.0
Hydrochloric acid	14.19	14.27	100.6
Phosphoric acid	42.72	42.82	100.3

Titration of a mixture containing a strong, weak, and very weak acid

Fig. 3 shows the potentiometric curve for titration of *p*-toluenesulfonic, propionic acid, and *p*-benzylphenol, which typify the strong, weak and very weak acids classifications. The first inflection represents the neutralization of *p*-toluenesulfonic acid, the second, propionic acid, and the third, *p*-benzylphenol. Table V indicates the results obtained on analysis of mixtures of these three acids.

DISCUSSION

This work does not purport to be a complete study of the analysis of any specific acid mixture. It does indicate, however, the feasibility of determining all types of acid mixtures by the differentiating titrations described and should suggest simple

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TABLE V

ANALYSIS OF *p*-TOLUENESULFONIC ACID, PROPIONIC ACID, AND *p*-BENZYLPHENOL MIXTURES

p-Toluenesulfonic acid		Recovery %	*Propionic acid*		Recovery %	*p-Benzylphenol*		Recovery %
Added mg	*Found mg*		*Added mg*	*Found mg*		*Added mg*	*Found mg*	
33.67	33.60	99.8	21.69	21.92	101.1	45.16	44.94	99.5
50.51	50.76	100.5	17.35	17.22	99.3	27.09	27.35	101.0
67.34	67.38	100.1	13.01	13.00	99.9	36.12	35.57	98.5
84.18	84.00	99.8	8.68	8.69	100.1	72.25	73.05	101.1
16.84	16.80	99.8	34.70	34.60	99.7	18.06	17.78	98.4

procedures for the analysis of acid mixtures now being determined by tedious and indirect methods.

Data on the differential titration of sulfuric acid–hydrochloric acid and sulfuric acid–nitric acid mixtures are not presented as a new alkalimetric method. The analysis of these acid mixtures with another titrant was reported by CRITCHFIELD AND JOHNSON[9], who reviewed the literature on this subject to 1954. The purpose of this work, as previously emphasized, is to indicate further the great versatility of tetrabutylammonium hydroxide as a titrant for acids and acid mixtures.

ACKNOWLEDGEMENT

The authors express their appreciation to A. J. SENSABAUGH for preparation of the figures.

SUMMARY

Strong acid mixtures as well as acid mixtures containing all classifications of acids can be analyzed by differentiating titrations in pyridine solution with 0.1*N* tetrabutylammonium hydroxide as the titrant. Included in the study are analyses of mixtures of sulfuric acid and nitric, hydrochloric, perchloric, phosphoric and sulfonic acids, respectively, as well as the resolution of a typical strong acid, weak acid and very weak acid mixture.

RÉSUMÉ

Des mélanges d'acides forts ont pu être dosée, dans la pyridine, par titrage différentiel, au moyen d'hydroxyde de tétrabutylammonium. On a pu également effectuer l'analyse de mélanges renfermant un acide fort, un acide faible et un acide très faible.

ZUSAMMENFASSUNG

Mischungen von starken Säuren, in Pyridin gelöst, können durch eine differenzierte Titration mit einer Standard-Tetrabutylammoniumhydroxydlösung analysiert werden. Die Methode lässt sich auch auf Gemische von starken, schwachen und sehr schwachen Säuren anwenden.

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HIGH FREQUENCY TITRATION AND ESTIMATION OF IONS

I. DETERMINATION OF SILVER

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Use of the high frequency titrimeter has attracted the attention of the analysts during the past few years and at present various types of chemical reactions are being studied with it. High frequency titrimetry has been found, as reported herein, to be a very useful technique for the estimation of silver with certain common organic and inorganic reagents. The end-point of the reactions has been found to be very sharp, stoichiometric and reproducible.

Apparatus

The apparatus used in the present investigation is a modification of that proposed by HALL[1]. The complete assembly is shown in the attached diagram (Fig. 1).

The cell containing the electrolytic solution was placed in parallel with the capacitor circuit. The frequency of 5.774 mega cycles/sec was produced by a piezo-electric quartz crystal. A change in the composition of the solution produced a change in the frequency, as a result of which, the oscillations of the quartz crystal stopped. Thus a change in capacity was necessary to restore the oscillations to their original value and these changes in capacity, following the change in composition of the solution, were noted and plotted against the volume in ml of the reagent added. Since the condenser dial readings were found to decrease linearly with the capacity of the condenser, dial readings were plotted, for the sake of convenience, against ml of the added electrolyte. The dial used was a slow motion vernier (Ormond) divided into 100 divisions.

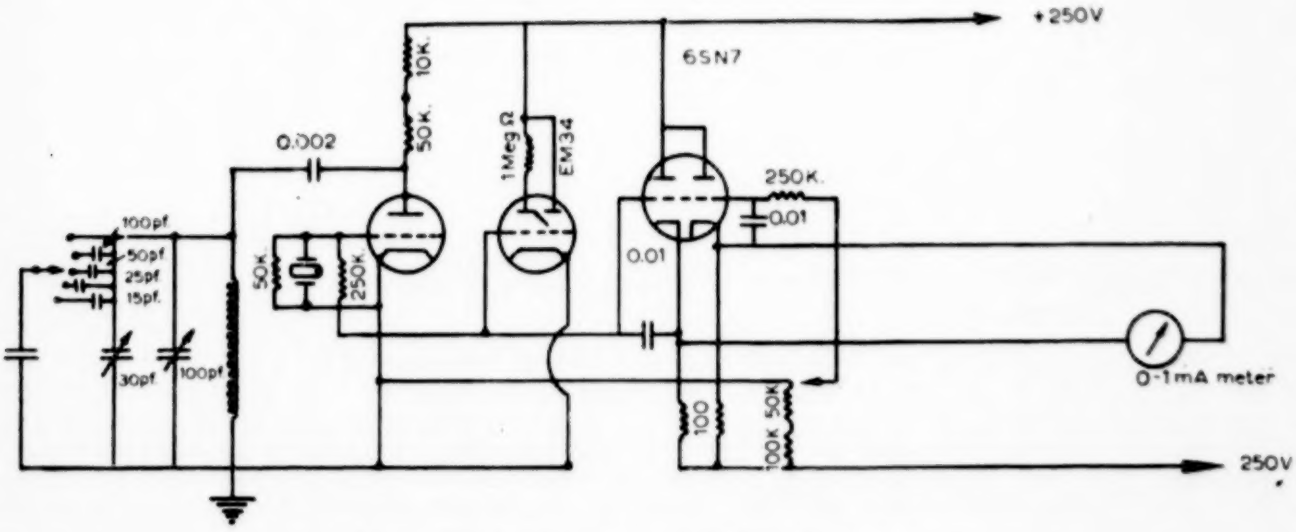

Fig. 1. High frequency titration apparatus.

EXPERIMENTAL

Materials

Doubly-distilled water is used throughout the course of the experiment. All chemicals used were of A.R. quality. Standard solutions of silver nitrate, potassium chloride, potassium bromide,

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potassium iodide, potassium chromate, ammonium thiocyanate and potassium cyanide were prepared by the usual methods.

A standard solution of bismuthiol I was prepared by dissolving a weighed quantity of this reagent in a definite volume of water, whereas those of bismuthiol II, 2-mercaptobenzothiazol and 2-mercaptobenzimidazole were prepared in ethyl alcohol.

Procedure

Silver has been estimated with potassium chloride, potassium bromide, potassium iodide, potassium cyanide, ammonium thiocyanate, potassium chromate and some organic reagents as bismuthiol I, bismuthiol II, 2-mercaptobenzimidazole and 2-mercaptobenzothiazole. The results are highly accurate except for those methods involving chromate, bismuthiol I and 2-mercaptobenzimidazole. The requisite amount of silver nitrate solution was placed in the titration cell and then diluted with water to 70 ml at which the height of the water was just sufficient to fill the cell to a level slightly above the upper metal band. The standard solution of the reagent was then added in small increments, over a range of several ml on both sides of the end-point, and the change in the condenser dial readings, after each addition, was noted. Potassium chloride, potassium bromide, potassium iodide and ammonium thiocyanate were found to behave similarly in that silver (1 to 50 mg) was accurately determined by their use (Fig. 2). However, low results were obtained when silver nitrate was titrated with potassium cyanide (see curves of Fig. 3). When the cyanide solution

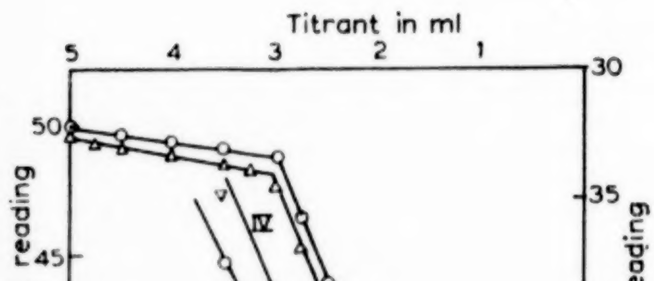

Fig. 2. Determination of silver. I: 10 ml $M/100$ $AgNO_3$ with $M/20$ KI; II: 10 ml $M/100$ $AgNO_3$ with $M/20$ KCl; III: 10 ml $M/100$ $AgNO_3$ with $M/20$ NH_4SCN; IV: 10 ml $M/100$ $AgNO_3$ with $M/20$ KBr.

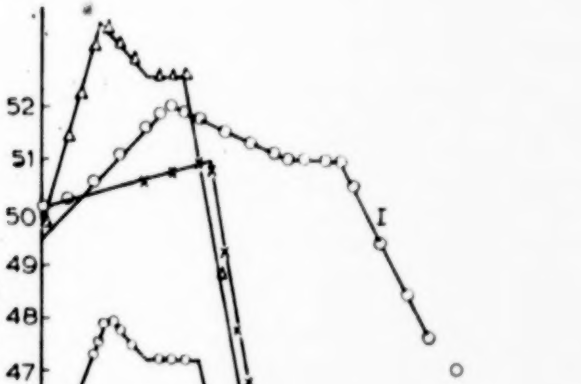

Fig. 3. Titration of I: 5 ml $M/20$ KCN with $M/20$ $AgNO_3$; II: 2.5 ml $M/20$ KCN with $M/20$ $AgNO_3$; III: 1.25 ml $M/20$ KCN with $M/40$ $AgNO_3$; IV: 20 ml $M/100$ $AgNO_3$ with $M/20$ KCN.

was taken in the titration cell and silver nitrate added the end-point corresponding to the formation of K[Ag(CN)$_2$] was found to be highly accurate. The second break in the curves was suggested to be due to the dissociation of the complex simply to AgCN; during direct titration, an end-point corresponding to the formation of simple AgCN was not obtained. Among the organic reagents employed, bismuthiol II and 2-mercaptobenzothiazole were found to give good results only when less than 15 mg of silver were present (Fig. 4). With higher amounts, results were not very good. Very low results were obtained with the reagents bismuthiol I and 2-mercaptobenzimidazole, since with their use precipitation of silver was not very rapid.

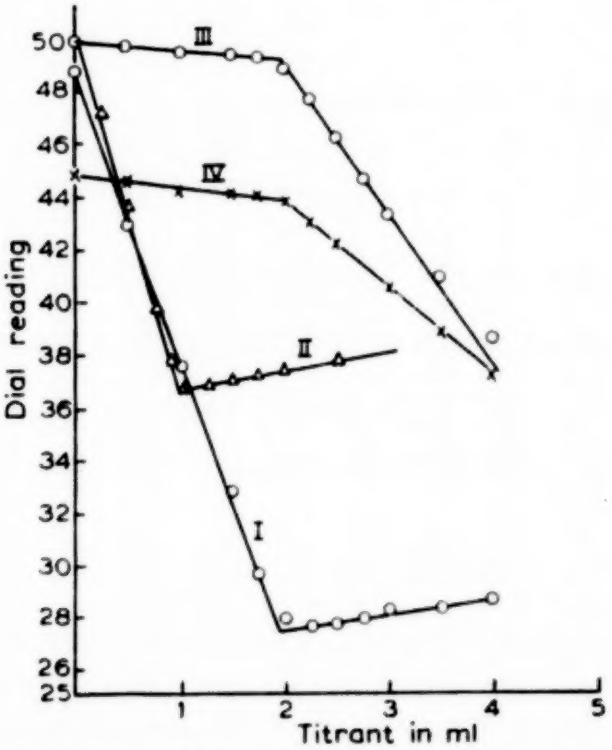

Fig. 4. Titration of I: 10 ml $M/100$ AgNO$_3$ with $M/20$ 2-mercaptobenzothiazole; II: 5 ml $M/100$ AgNO$_3$ with $M/20$ 2-mercaptobenzothiazole; III: 10 ml $M/100$ AgNO$_3$ with $M/20$ bismuthiol II; IV: 5 ml $M/100$ AgNO$_3$ with $M/40$ bismuthiol II.

ACKNOWLEDGEMENTS

Our grateful thanks are due to University Grants Commission, Government of India, for providing us with the funds for the construction of the high frequency titration apparatus.

SUMMARY

High frequency titration has been found to be a highly suitable technique for the volumetric estimation of silver with potassium chloride, potassium bromide, potassium iodide, ammonium thiocyanate, 2-mercaptobenzothiazole and bismuthiol II. The results have been accurate when the amount of silver present was not more than 15 mg. Titration of potassium cyanide with silver nitrate gives an end-point corresponding to the complex K[Ag(CN)$_2$]. Reverse titration fails to give any sharp break. Mercaptobenzimidazole, bismuthiol I and potassium chromate were not suitable reagents in these determinations.

RÉSUMÉ

La technique de titrage à haute fréquence convient très bien au dosage volumétrique de l'argent au moyen de chlorure de potassium, de bromure de potassium, d'iodure de potassium, de thiocyanate d'ammonium, le mercapto-2-benzothiazole et le bismuthiol II. Pour des quantités d'argent inférieures à 15 mg, la précision des résultats est excellente.

ZUSAMMENFASSUNG

Die Methoden der Hochfrequenztitration eigen sich sehr gut zur volumetrischen Bestimmung von Silber mit Hilfe einer Lösung von Kaliumchlorid, Kaliumbromid, Kaliumjodid, Ammoniumthiocyanat, 2-Mercaptobenzothiazol und Wismuthiol II. Bei Mengen von weniger als 15 mg Silber werden sehr gute Resultate erhalten.

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SEPARATIONS INVOLVING SULPHIDES

III. SEPARATION OF MOLYBDENUM AND TELLURIUM FROM BARIUM

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In a previous publication[1] in this series, methods were proposed for the quantitative separation of selenium, arsenic, antimony and mercury from barium. These methods are based upon the formation and subsequent decomposition of thiosalts. In this paper a description is given of the successful separation of molybdenum and tellurium from barium by means of this method.

EXPERIMENTAL

Reagents

Ammonium molybdate (Kahlbaum), barium chloride (AnalaR), potassium tellurite, sodium sulphide 2*N*, hydrochloric acid 2*N*.

Separation of molybdenum from barium

The mixture (in HCl) was treated with a large excess of sodium sulphide reagent (the reagent must be added in small quantities at a time with constant shaking to avoid the formation of molybdenum blue), acidified with hydrochloric acid, heated to boiling, and allowed to cool to room temperature. The precipitate of molybdenum trisulphide was filtered through a weighed sintered glass crucible (porosity 4) washed thoroughly with water, and then with alcohol and ether, sucked dry at the filter pump for 15 min, dried in a vacuum desiccator for an hour and weighed as $MoS_3 \cdot 2H_2O$. In the filtrate barium was estimated as sulphate. The results are given in Table I.

TABLE I

SEPARATION OF MOLYBDENUM FROM BARIUM WITH 2*N* SODIUM SULPHIDE REAGENT

Wt. of Mo as found in the ppt. $MoS_3 \cdot 2H_2O$ g	*Wt. of Mo actually present* g	*Wt. of Ba as found in the ppt.* $BaSO_4$ g	*Wt. of Ba actually present* g
0.04758	0.04760	0.1756	0.1756
0.03811	0.03808	0.09640	0.09656
0.05163	0.05154	0.1353	0.1352

Separation of tellurium from barium

The mixture was treated as for the separation Mo–Ba. The precipitate of tellurium sulphide was dried at 100–105° for an hour and weighed as TeS_2. In the filtrate barium was estimated as sulphate. The results are given in Table II.

TABLE II

SEPARATION OF TELLURIUM FROM BARIUM WITH 2*N* SODIUM SULPHIDE REAGENT

Wt. of Te as found in the ppt. TeS_2 g	*Wt. of Te actually present* g	*Wt. of Ba as found in the ppt.* $BaSO_4$ g	*Wt. of Ba actually present* g
0.1180	0.1180	0.1412	0.1412
0.1181	0.1180	0.05637	0.05649
0.04736	0.04720	0.1411	0.1412

ACKNOWLEDGEMENTS

This work was carried out in the Chemical Laboratories, University of Allahabad. The author is grateful to Prof. Dr. S. Ghosh and Dr. I. K. Taimni for their kind interest.

SUMMARY

It has been shown that the method of separating of molybdenum and tellurium from barium, based on the decomposition of thiosalts, gives fairly correct results in quantitative analysis.

RÉSUMÉ

Les séparations du molybdène et du tellure, d'avec le baryum, basées sur la décomposition des thiosels donnent de bons résultats en analyse quantitative.

ZUSAMMENFASSUNG

Es wurde gezeigt, dass die Trennungen von Molybdän und Tellur vom Barium auf Grund der Zersetzung der Thiosalze bei der quantitativen Analyse recht gute Resultate ergeben.

LITERATUR

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SEPARATIONS INVOLVING SULPHIDES

IV. SEPARATION OF ARSENIC, ANTIMONY, TELLURIUM AND MERCURY FROM ZIRCONIUM

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In earlier publications[1,2] in this series, methods were proposed for the quantitative separation of the metals of the arsenic group from barium. These methods are based upon the formation and subsequent decomposition of thiosalts. In this paper, a description is given of the successful separation of arsenic, antimony, tellurium and mercury from zirconium by means of this method.

In the following series of experiments the mixture containing the two metals is treated, if necessary, with sodium hydroxide and tartrate to keep zirconium in solution, and then an excess of the alkali sulphide reagent is added, whereby the metals of the arsenic group form thiosalts. These are decomposed with a measured volume of hydrochloric acid, sufficient to make the concentration of acid in the resulting mixture higher than 1*N*. The metals are then separated and estimated as sulphides. Zirconium is precipitated from the filtrate with cupferron and estimated as ZrO_2.

EXPERIMENTAL

Reagents

Sodium arsenate, zirconium oxychloride, sodium hydroxide, sodium tartrate (AnalaR), sodium sulphide 2*N*, hydrochloric acid, antimony potassium tartrate (AnalaR), potassium tellurite, mercuric chloride (AnalaR).

Separation of arsenic from zirconium

Measured portions of standard solutions of salts of these metals are mixed together, and, in order to keep zirconium in solution, the precipitate of zirconium arsenate is dissolved by treatment with sodium hydroxide and tartrate. Then the mixture is treated with a large excess of sodium sulphide reagent and acidified with a measured quantity of conc. hydrochloric acid sufficient to make the concentration of acid in the resulting mixture approximately 6*N*. The mixture is heated to boiling, stirred and allowed to cool to room temperature. The precipitate of As_2S_5 is filtered through a weighed sintered glass crucible (porosity 4), washed thoroughly with *N* HCl, water, and alcohol, dried at 100–110° for an hour and weighed as As_2S_5.

After expelling the hydrogen sulphide gas from the filtrate and adding sulphuric acid to a concentration of about 10%, zirconium is precipitated by cupferron, ignited, and weighed as ZrO_2.

The results are given in Table I.

TABLE I

SEPARATION OF ARSENIC FROM ZIRCONIUM WITH 2N SODIUM SULPHIDE REAGENT

Wt. of As as found in the ppt. As_2S_3 g	*Wt. of As actually present* g	*Wt. of Zr as found in the ppt.* ZrO_2 g	*Wt. of Zr actually present* g
0.05694	0.05694	0.04130	0.04109
0.04564	0.04555	0.04116	0.04109
0.02046	0.02050	0.03279	0.03287

Separation of antimony from zirconium

Proceed as for As–Zr but acidify with a measured quantity of 3N hydrochloric acid sufficient to make the concentration of acid in the resulting mixture 1–1.2N. The precipitate of antimony sulphide thus obtained is filtered and weighed as Sb_2S_3. In the filtrate zirconium is precipitated by cupferron, ignited and weighed as ZrO_2. The results are given in Table II.

TABLE II

SEPARATION OF ANTIMONY FROM ZIRCONIUM WITH 2N SODIUM SULPHIDE REAGENT

Wt. of Sb as found in the ppt. Sb_2S_3 g	*Wt. of Sb actually present* g	*Wt. of Zr as found in the ppt.* ZrO_2 g	*Wt. of Zr actually present* g
0.08876	0.08875	0.04102	0.04109
0.08876	0.08875	0.03287	0.03287
0.03556	0.03550	0.03301	0.03287

Separation of tellurium from zirconium

Treat the mixture as for Sb–Zr in order to precipitate tellurium as the sulphide; this is filtered and weighed as TeS_2. In the filtrate zirconium is precipitated by cupferron, ignited, and weighed as ZrO_2. The results are given in Table III.

TABLE III

SEPARATION OF TELLURIUM FROM ZIRCONIUM WITH 2N SODIUM SULPHIDE REAGENT

Wt. of Te as found in the ppt. TeS_2 g	*Wt. of Te actually present* g	*Wt. of Zr as found in the ppt.* ZrO_2 g	*Wt. of Zr actually present* g
0.06247	0.06250	0.04102	0.04109
0.06261	0.06250	0.03279	0.03287
0.04982	0.0500	0.03287	0.03287

Separation of mercury from zirconium

The mixture is treated as usual to precipitate mercury as sulphide, which is then filtered and weighed as HgS. In the filtrate zirconium is precipitated by cupferron, ignited and weighed as ZrO_2.

The results are given in Table IV.

TABLE IV

SEPARATION OF MERCURY FROM ZIRCONIUM WITH 2*N* SODIUM SULPHIDE REAGENT

Wt. of Hg as found in the ppt. HgS g	*Wt. of Hg actually present* g	*Wt. of Zr as found in the ppt. ZrO_2* g	*Wt. of Zr actually present* g
0.1876	0.1875	0.04116	0.04109
0.1741	0.1740	0.04109	0.04109
0.1740	0.1740	0.03279	0.03287

Notes on negative results

Negative results have been obtained in the following cases:

(A) Selenium and zirconium,

(B) Tin and zirconium.

(A) *Selenium and zirconium:* When attempts are made to separate selenium from a mixture containing the two metals and to estimate it as sulphide, high results are obtained. This is probably due to zirconium ions being absorbed by the selenium sulphide precipitate. Even the character of the precipitate is changed; instead of an orange-red spongy mass a yellow substance is obtained, which is much more fragile. However, tartrate, used to keep zirconium in solution, does not interfere with the precipitation of pure selenium sulphide.

(B) *Tin and zirconium:* When tin is separated from a mixture containing zirconium and estimated as sulphide by decomposing its thiosalt, with acids (2*N*, 8*N*, 10*N* glacial acetic acid and 2*N* HCl) high results are obtained. This is due to the coprecipitation of zirconium with tin sulphide. Tartrate cannot be used to dissolve the zirconium, as it inhibits the precipitation of tin sulphide.

ACKNOWLEDGEMENTS

This work was carried out in the Chemical Laboratories, University of Allahabad. The author is grateful to Prof. Dr. S. GHOSH and Dr. I. K. TAIMNI for their kind interest.

SUMMARY

It has been shown that the methods for separating arsenic, antimony, tellurium, and mercury from zirconium, based on the decomposition of thiosalts, give fairly correct results in quantitative analysis. However, the method fails in the following combinations of metals: (1) selenium and zirconium, (2) tin and zirconium.

RÉSUMÉ

Les séparations de l'arsenic, de l'antimoine, du tellure et du mercure d'avec le zirconium, basées sur la décomposition des thiosels, donnent de bons résultats en analyse quantitative. Cependant cette méthode ne peut pas être utilisée pour les séparations suivantes: (1) sélénium et zirconium, (2) étain et zirconium.

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ZUSAMMENFASSUNG

Es wurde gezeigt, dass die Trennungen von Arsen, Antimon, Tellur und Quecksilber vom Zirkonium, welche sich auf die Zerstörung der Thiosalze gründen, bei der quantitativen Analyse recht gute Resultate geben. Die Methode versagt aber bei den folgenden Kombinationen: 1. Selen und Zirkonium, 2. Zinn und Zirkonium.

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THE DETERMINATION OF MOLECULAR WEIGHT USING THERMISTORS

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It has been demonstrated by Hill[1] that a solution when exposed to vapor of the same solvent assumes some temperature higher than that of solvent alone exposed to the same vapor. This temperature difference is due to vapor condensation on the solution whereas the solvent being subject to equal rates of evaporation and condensation remains at the temperature of the vapor.

This principle has been applied by Müller and Stolten[2] to the determination of molecular weight by using thermistors as the temperature sensing elements and stainless steel cups to hold the solvent and solution. They found that approximately 30 min is required for the stainless steel cup and solution therein to reach a maximum temperature.

The principal modifications of the apparatus used here permit the solution to

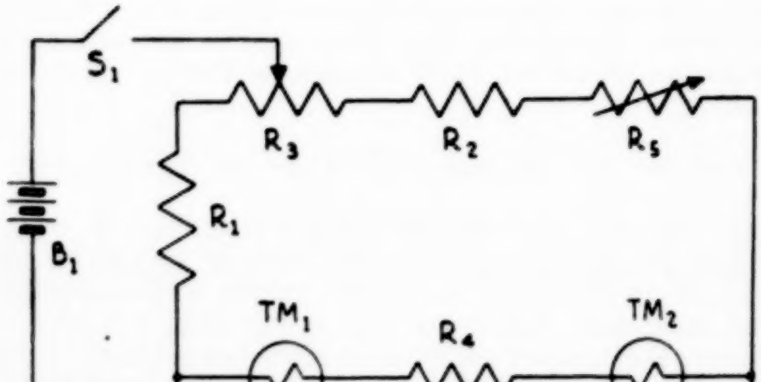

Fig. 1. Wheatstone bridge circuit.

reach its maximum temperature in about 3 min, make possible a substantial temperature rise of the solution for a given solute concentration and allow convenient and rapid determination of the molecular weight of successive samples.

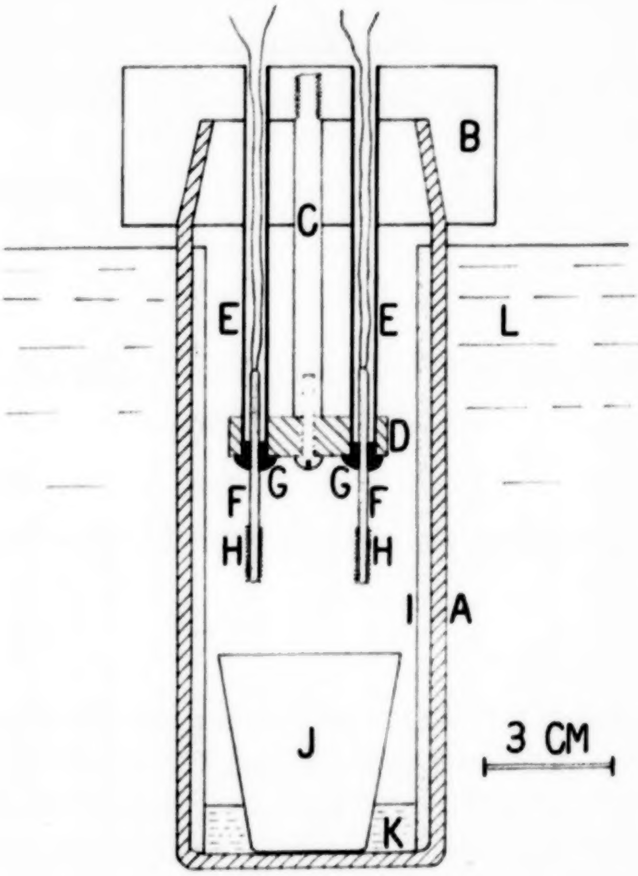

Fig. 2. Solvent-vapor chamber *vs.* thermistor assembly.

APPARATUS

The Wheatstone bridge circuit used in these experiments is shown in Fig. 1. The various components of the circuit are as follows:
B_1: 4.5 Volt battery; S_1: Single-pole, single-throw switch; R_1 and R_2: 100,000 ohm wire-wound fixed resistors; R_3: 1,000 ohm wire-wound variable resistor; R_4: 20 ohm wire-wound variable resistor; R_5: 1,000 ohm ten-turn, wire-wound micropotentiometer; TM_1 and TM_2: Type GA51P8 thermistors made by Fenwal Electronics, Inc., Framingham, Massachusetts; M_1: 0 to 50 microammeter; M_2: Null Detector Model No. 104WIG made by the Minneapolis-Honeywell Regulator Co., Minneapolis, Minnesota.

The solvent-vapor chamber and thermistor assembly are shown in Fig. 2. The various parts are as follows:
A: Glass solvent-vapor chamber; B: "Bakelite" cap machined to fit § 71/25 glass joint; C: 6 mm stainless steel rod support for thermistor assembly; D: "Teflon" thermistor support; E: 5-mm glass tubing; F: Fenwal Type GA51P8 thermistors; G: Cupric oxide–phosphoric acid cement; H: 40-turn platinum wire coils made with 0.3-mm diameter wire; I: 3 mm thick absorbent paper lining the total depth and about 3/4 of the circumference of the inner chamber wall and covered on both sides with 1.5-mm mesh aluminum screen; J: Stainless steel crucible; K: Solvent; L: Constant temperature water bath.

PROCEDURE

Immerse the apparatus of Fig. 2 in a water bath thermostated at about 30° + 0.01°. Pour solvent into the vapor chamber so that there is about 1 cm of excess solvent in the bottom of the chamber over that required to saturate the absorbent paper

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lining the inside wall of the chamber. Rinse off both platinum wire coils covering the thermistors with about 0.1 to 0.2 ml of solvent. The solvent can be readily placed on the coils by means of an elongated medicine dropper inserted into the vapor chamber through a hole in the "Bakelite" cap. The medicine dropper is stored, when not in use, in copper tubing which is sealed on the bottom and immersed in the water bath. Set the micropotentiometer R_5 of Fig. 1 at zero resistance and turn on switch S_1 of Fig. 1. When temperature equilibrium has been established within the vapor chamber, balance the bridge using resistors R_3 and R_4 of Fig. 1. Replace the solvent in contact with the sensing thermistor TM_1 of Fig. 1 by rinsing with 0.1 to 0.2 ml of solution which has been previously brought to 30° by immersion of its container in the water bath. Balance the bridge using the 1,000 ohm micropotentiometer.

Approximately 3 min are required for the sensing thermistor to reach its maximum temperature. Record the maximum resistance of the micropotentiometer and use this value to calculate the molecular weight of the solute (see below). Rinse off the sensing thermistor with solvent and return the micropotentiometer to zero resistance. Temperature equilibrium will again be established in about 3 min at which time the molecular weight of the next sample may be determined. If desired, the sample may be recovered from the stainless steel crucible within the solvent-vapor chamber.

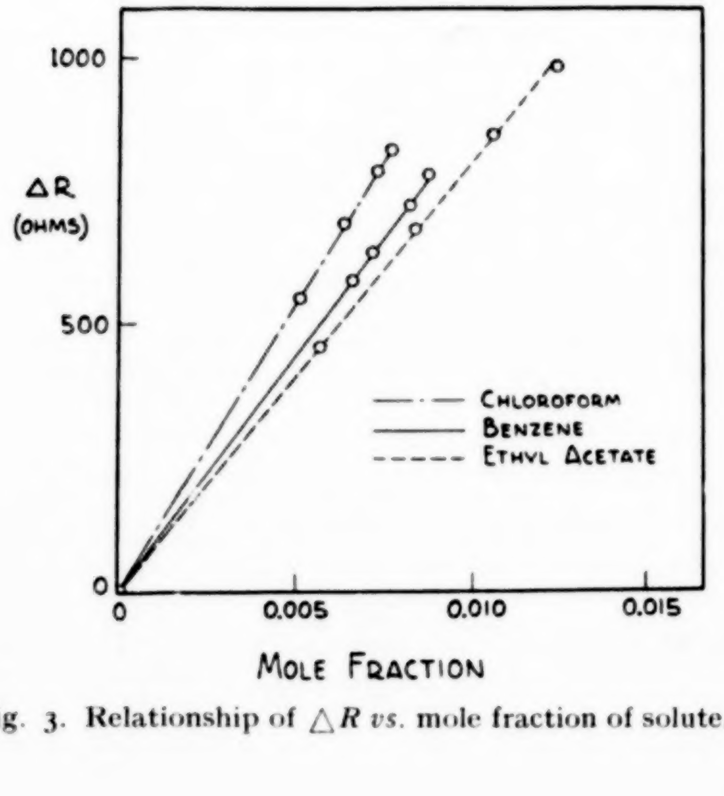

Fig. 3. Relationship of $\triangle R$ *vs.* mole fraction of solute.

Calculation

Thermistor resistance varies logarithmically with temperature but only a maximum of approximately 1% of the total resistance of one of the thermistors is utilized in these experiments so $\triangle T$ is essentially proportional to $\triangle R$. It is also true that $\triangle R = K \cdot MF$ (see Fig. 3), where $\triangle T$ and $\triangle R$ are the changes in temperature and resistance, respectively, of the sensing thermistors, K is a proportionality constant

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and MF is the mole fraction of solution. Substituting the appropriate terms for MF and rearranging yields the equation:

$$MW_{\text{solute}} = \frac{g_{\text{solute}} \cdot MW_{\text{solvent}}(K - \triangle R)}{\triangle R \cdot g_{\text{solvent}}}$$

where MW is molecular weight and g is weight in grams.

RESULTS

The molecular weights of 4 different compounds in three different solvents, as found by using the above procedure, are given in Table I.

The values of K listed in Table I are obtained from the slopes of the lines of plots of $\triangle R$ *versus* mole fraction of solute (Fig. 3).

The average deviation of a single determination of $\triangle R$ is between 3 and 4 ohms. This value was obtained by 30 consecutive determinations of the $\triangle R$ value of the same solution.

TABLE I

MOLECULAR WEIGHT DETERMINATIONS

Solvent: Benzene, $K = 88{,}700$

Compound	ΔR	*Mole fraction*	*Molecular (found)*	*Weight (theor)*
Naphthalene	777	0.00866	127	128
1,2,4,5-Tetrachlorobenzene	633	0.00712	215	216
Dibenzyl	581	0.00659	183	182
Coumarin	723	0.00823	148	146

Solvent: Ethyl Acetate, $K = 80{,}400$

Compound	ΔR	*Mole fraction*	*Molecular (found)*	*Weight (theor)*
Naphthalene	981	0.01230	129	128
1,2,4,5-Tetrachlorobenzene	453	0.00568	218	216
Dibenzyl	681	0.00835	179	182
Coumarin	855	0.01063	146	146

Solvent: Chloroform, $K = 107{,}900$

Compound	ΔR	*Mole fraction*	*Molecular (found)*	*Weight (theor)*
Naphthalene	779	0.00728	129	128
1,2,4,5-Tetrachlorobenzene	545	0.00505	216	216
Dibenzyl	684	0.00632	182	182
Coumarin	825	0.00761	145	146

DISCUSSION

The thermistors shown in Figs. 1 and 2 are nominally rated at 100,000 ohms at 25° and have a negative temperature coefficient of about 4.6%.

The bridge null detector is conservatively rated as having a sensitivity of 0.001 μA/mm so a 1 to 2 ohm unbalance in one arm of the bridge corresponding to about 10^{-10} A bridge unbalance can be detected.

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The water bath temperature need not be controlled closer than 0.01°. Assuming the reference and sensing thermistors are matched within 2000 ohms, a change in temperature of 0.01° within the vapor chamber will result in a bridge unbalance of approximately one ohm (calculated). Furthermore, water bath temperature fluctuations are damped before reaching the inside of the vapor chamber by the glass wall of the vapor chamber.

The purpose of the aluminum screen covering the surface of the absorbent paper within the vapor chamber is to help equalize temperature within the chamber.

It appears likely that solvents other than the three listed in the previous experiments could be used for the determination of molecular weight. Thus far, one or more of the three solvents has been suitable for determination of the molecular weight of samples dealt with by this laboratory.

Molecular weights as high as 2000 have been determined by this method. If 10% is set as the maximum useable concentration of solution and 350 ohms is chosen as the smallest value of $\triangle R$ which can be determined with a relative error of less than 2%, the method is sufficiently sensitive using chloroform as solvent to determine molecular weights up to about 3500.

The temperature rise of solutions of the solutes listed in Table I is only about 90% of the maximum theoretical temperature rise, but because the geometry of the thermistors in the solvent-vapor chamber is fixed, reproducible results are obtained.

SUMMARY

A method of less than 2% relative error, requiring less than 5 mg of sample and utilizing thermistors is described for the rapid determination of molecular weight.

RÉSUMÉ

Une méthode rapide est proposée pour la détermination de poids moléculaires permettant des mesures sur des quantités de substances inférieures à 5 mg.

ZUSAMMENFASSUNG

Es wird eine rasche Methode zur Molekulargewichtsbestimmung von Milligrammengen unter Anwendung von Thermistoren beschrieben.

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INDIRECT EDTA-TITRATION OF ALUMINIUM WITH LEAD(II) SOLUTIONS AND 4-(2-PYRIDYLAZO)-RESORCINOL (PAR) AS INDICATOR

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A problem of considerable importance in the field of inorganic analytical chemistry is to find improved methods for the determination of aluminium. The introduction of EDTA offers the possibility of titrating aluminium. A number of papers on this subject have been published, but it has proved difficult to find satisfactory methods for the direct EDTA-titration of aluminium, and only a few such methods have been suggested. On the other hand, a series of publications describe indirect methods of determination using different indicators and standard solutions for back titration of excess EDTA.

An excellent survey of the literature on EDTA-titration of aluminium (and other metals) has been published by Flaschka, Barnard and Broad[1].

In a paper recently published by Honda, Körbl, Bažant and Přibil[2], aluminium is indirectly determined with standard solutions of lead(II) and xylenol orange as indicator.

In another paper, Wehber[3] mentions that 4-(2-pyridylazo)-resorcinol (PAR) is an excellent indicator for metals and that a sharp end-point from red to yellow is obtained when lead(II)-solutions are titrated with EDTA. Wehber does not, however, give any details about the procedure used or the results obtained.

In the present publication, the EDTA-titration of lead(II) with PAR as indicator is investigated, and the application of lead(II) standard solutions and PAR is introduced for indirect determination of macro and micro amounts of aluminium.

EXPERIMENTAL

Preparation of PAR

4-(2-pyridylazo)-resorcinol is synthesized according to a procedure described by Chichibabin[4]. The indicator can now also be purchased from chemical firms.

PAR solution

A 0.1% solution in distilled water of the sodium salt is applied. This solution can be stored for months.

Standard solutions

EDTA standard solution. 0.05*M* EDTA solution is prepared by dissolving 18.61 g of ethylenediaminetetraacetic acid, disodium salt, in distilled water and diluting to 1000 ml. This solution is standardized against the lead standard solution mentioned below. The molarity was 0.05004. A 0.001*M* EDTA solution is prepared by dilution.

Aluminium standard solution. 10.000 g of aluminium (super pure — 99.997% Al) are dissolved in 1:1 hydrochloric acid and diluted to 1000 ml. The pH of this solution is about 2.

Lead standard solution. A $0.05M$ lead(II) solution is prepared by dissolving 10.360 g of high purity (spectrographically standardized) in nitric acid and diluting to 1000 ml.

All other chemicals used are of analyzed reagent quality.

For the determination and regulation of pH, indicator papers are normally employed. For some pH determinations, a Beckman pH-meter model H2 is employed.

Titration of lead(II) with EDTA and PAR

Known amounts of lead are titrated with $0.001M$ EDTA at pH 5–7.

When a neutral, unbuffered solution of lead is titrated with EDTA, the pH will decrease owing to the release of hydrogen ions. Below pH 5, the end-point of the titration is obscure and appears before the equivalence point is reached.

In order to adjust the pH to 6.5–7 before the equivalence point is reached, a few drops of ammonia solution are added. The correct pH is controlled with indicator paper. If ammonia is added before the addition of EDTA, precipitation takes place. The precipitate is slowly redissolved in EDTA.

In Table I the results of a series of titrations of known amounts of lead(II) are given.

TABLE I

TITRATION OF LEAD(II) WITH $0.001M$ EDTA SOLUTION AND PAR

Volume of solution before titration about 100 ml

Pb taken mg	*EDTA used ml*	*Pb found mg*	*Error relative %*
5.180	24.98	5.176	−0.1
5.180	25.03	5.186	+0.1
5.180	24.97	5.174	−0.1
5.180	25.02	5.183	+0.06
5.180	25.01	5.182	+0.04

The end-point is reached when the colour changes from red to yellow-orange. The end-point is sharp and permits the use of highly diluted EDTA solutions.

Indirect determination of aluminium with EDTA, lead(II) and PAR

Known amounts of aluminium are taken, an excess of EDTA is added and back titration is carried out with lead(II) and PAR.

The reaction between aluminium and EDTA is quantitative (under these circumstances) at room temperature and at the pH of the aluminium standard solution (*viz.*, about pH 2). After the addition of $0.05M$ EDTA, the solution is diluted to about 100 ml, the pH is adjusted to 6.5–7 with ammonia solution and $0.05M$ lead(II) solution and PAR is employed for back titration. Before the end-point is reached, the pH is again adjusted. The final end-point is seen by a sharp colour change from yellow to yellow-orange.

In Table II, the results of a series of indirect determinations of aluminium are given.

Table III shows that micro amounts of aluminium also can be determined with a relatively high degree of accuracy. In this case, $0.001M$ solutions of EDTA and lead(II) are utilized.

TABLE II

INDIRECT DETERMINATION OF ALUMINIUM WITH 0.05004 *M* EDTA SOLUTION, 0.05 *M* LEAD(II) SOLUTION AND PAR

Volume of solution before back titration about 100 ml

Al taken mg	*EDTA added ml*	*Pb(II) used ml*	*Al found mg*	*Error relative %*
25.00	25.00	17.52	25.00	±0.0
25.00	25.00	17.50	25.00	±0.0
25.00	30.00	30.90	25.07	+0.3
25.00	20.00	3.95	25.02	+0.1
25.00	21.00	6.78	24.96	−0.2
25.00	22.00	9.29	25.06	+0.2

TABLE III

INDIRECT DETERMINATION OF MICRO AMOUNTS OF ALUMINIUM WITH 0.001 *M* EDTA SOLUTION, 0.001 *M* LEAD(II) SOLUTION AND PAR

Al taken mg	*EDTA added ml*	*Pb(II) used ml*	*Al found mg*	*Error relative %*
0.674	50.00	24.97	0.675	+0.1
0.674	50.00	25.08	0.672	−0.3
0.674	50.00	25.02	0.674	±0.0
0.674	35.00	9.88	0.677	+0.4
0.674	35.00	10.00	0.674	±0.0
0.674	35.00	10.01	0.674	±0.0

The end-point is again taken when the colour changes from yellow to yellow-orange.

Influence of pH

The stability constants of the aluminium- and lead(II)-EDTA complexes are $10^{16.13}$ and $10^{18.04}$ respectively. Owing to the difference of stability, the following substitution reaction may take place when a small excess of lead(II) solution is added at the end-point of the back titration:

$$\mathrm{Al\ EDTA^{-} + Pb^{+2} \rightleftharpoons Pb\ EDTA^{-2} + Al^{+3}}$$

This reaction is pronounced at pH values above 7 and does not permit ready observation of the end-point. As mentioned above, it is also found that at pH values below 5, lead(II) ions do not form a coloured complex with PAR.

Consequently, the back titration is carried out at a pH between 5 and 7.

In order to keep the pH constant during the back titration, some conventional buffers were tested. Buffers containing organic acids unfavourably influenced the end-point. The application of a phosphate buffer completely decoloured the indicator before back titration. The use of ammonia in combination with indicator papers for regulation and control of pH is preferred.

The formation of hydroxy compounds of aluminium is avoided by keeping the pH of the aluminium standard solution at or below 2, and by adding excess EDTA before pH is increased.

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The influence of foreign ions on the complex formations between aluminium and EDTA

It is stated by HONDA and coworkers[2] that the rate of reaction between aluminium and EDTA is reduced appreciably in the presence of higher concentrations of foreign ions. In these cases, the rate of reaction can be increased by heating the aluminium solution after the addition of EDTA.

In Table IV a few titrations of small amounts of aluminium are carried out in the presence of higher concentrations of ammonium chloride and sodium nitrate. It is seen that in the presence of ammonium chloride the correct amount of aluminium can be found by heating the solution to boiling before back titration. On the other hand, when sodium nitrate is present, heating does not improve the accuracy.

TABLE IV

INDIRECT DETERMINATION OF ALUMINIUM WITH 0.001 *M* EDTA, 0.001 *M* LEAD(II) AND PAR IN IN THE PRESENCE OF FOREIGN IONS

0.674 mg Al taken. 30.00 ml EDTA added. Volume of solution about 100 ml pH 6–7.

Ions present	*Al found mg*	*Error relative %*	*Remarks*
10 g NH_4Cl	0.666	−1.2	No heating before back titration
10 g NH_4Cl	0.673	−0.1	Heated before back titration
10 g $NaNO_3$	0.638	−5.3	No heating before back titration
10 g $NaNO_3$	0.640	−5.0	Heated before back titration

SUMMARY

Indirect EDTA-titration of macro and micro amounts of aluminium is carried out with the utilization of standard solutions of lead(II) for back titration and 4-(2-pyridylazo)-resorcinol (PAR) als indicator.

RÉSUMÉ

Une méthode est proposée pour le dosage de l'aluminium au moyen de l'acide éthylènediaminotétracétique par titrage indirect avec une solution étalon de plomb.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von Aluminium mit Hilfe von Aethylendiaminotetraessigsäure durch indirekte Titration mit einer Bleisalzlösung.

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A NEW RAPID TITRIMETRIC METHOD FOR COPPER

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INTRODUCTION

A wide variety of methods is available for the determination of copper[1,2], but they are too time-consuming in as much as they require elaborate procedures. The credit of first working out a rapid and simple method goes to RHEAD[3]. This method consists in reducing an acid solution of the cupric salt by direct titration with titanous chloride in the presence of a sufficient quantity of thiocyanate. A few drops of ferrous solution added to the copper solution give a red coloration due to oxidation of iron(II) to iron(III) by copper(II). The titration is continued until the colour is pure white. The method was further investigated by THORNTON[4], MACH AND LEDERLE[5] AND KOLTHOFF[6]. This method, though quite suitable for rapid routine estimation of copper has the drawback that it required titanous chloride which is expensive.

The present investigation is based on the reduction of a hydrochloric acid solution of cupric copper by stannous chloride in the presence of thiocyanate. A few drops of ammonium molybdate solution served as the indicator. Ammonium molybdate gives an intense red colour in the presence of thiocyanate when reduced by stannous chloride. This colour change is reversible, though slow, in the presence of cupric solution. In the presence of copper, the molybdate is reduced only after all the copper has reacted. In practice, however, the colour change at the end-point is from pale rose to red-brown, probably due to traces of iron in the hydrochloric acid used. Though the colour change is not sharp, it is discernible to a careful observer without difficulty.

Stannous chloride possesses a low oxidation potential ($Sn^{+2} \rightleftharpoons Sn^{+4} + 2e$, $E_0 = -0.14$ V) and hence is a strong reducing agent. Lack of suitable indicators was responsible for its limited practical application until MÜLLER AND GÖRNE[7] made use of the potentiometric method for carrying out a series of titrations. They investigated the determination of iodine, ferric salts, dichromate, ferricyanide, gold(III), platinum(IV), mercuric salts and permanganate by means of stannous chloride. SZABO AND SUGAR[8] developed indicator methods for the determination of ferric, ferrous, dichromate, vanadate, iodate, bromate and ferricyanide ions, and for iodine by direct titration with stannous chloride.

REAGENTS

(1) Ammonium molybdate, A.R., 2% aqueous solution. (2) Copper sulphate, A.R., 0.1 *N*. (3) Stannous chloride, A.R., 0.1 *N*: 12 g of crystalline stannous chloride and 80 ml of conc. hydrochloric acid are used per l. The solution is prepared according to the procedure outlined by SZABO AND SUGAR[8]. The solution is stored under CO_2 in an apparatus described by SCOTT AND FURMAN[9]. (4) Hydrochloric acid, A.R., 1 : 1. (5) Potassium thiocyanate, pure, Merck, 10% aqueous solution. (6) Potassium bromate, A.R., 0.1 *N* solution. (7) Quinoline yellow, 0.2% aqueous solution.

RECOMMENDED PROCEDURE

Pipette 25 ml of the copper solution into a 300-ml Erlenmeyer flask, dilute with 75 ml of distilled water, add 10 to 15 ml of 1:1 hydrochloric acid followed by 5 drops of ammonium molybdate solution and 15 to 20 ml of thiocyanate solution. Add a pinch of sodium bicarbonate and immediately titrate with stannous chloride solution. Cuprous thiocyanate is precipitated and the colour of the contents of the flask turns to a pale rose when the end-point is being approached. Near the end-point add the stannous chloride solution slowly since the reaction does not appear to be instantaneous. At the end-point, the colour of the solution changes from pale rose or pink to red-brown. The volume of the solution being titrated should not be less than 130 ml or more than 200 ml. Standardize the stannous chloride with standard potassium bromate solution using 1 drop of quinoline yellow as the indicator. This titration should be carried out in an atmosphere of carbon dioxide.

EXPERIMENTAL

The stock solution of copper sulphate was standardized iodometrically according to the procedure described by VOGEL[1] (p. 411). The thiosulphate solution was standardized with standard potassium bromate solution. The same potassium bromate was also used for standardizing the stannous chloride solution. Various known volumes of the stock solution of copper sulphate were run from a burette into a conical flask and titrated with stannous chloride as described previously. These titrations were carried out under an atmosphere of carbon dioxide drawn from a cylinder. The copper content in each case was calculated from the titre of the stannous chloride and compared with that obtained iodometrically. The range and accuracy of the method are shown in Table I. Table II shows the precision of the method under the best conditions, determined according to the procedure outlined by MORAN[10]. Since the $X_1 \pm LU_{av}$ does not embrace the known value, the method is not very accurate. But since the error involved is within 0.5%, the method is recommended for routine technical analyses where an accuracy of the order of 1% is sufficient. The advantages of the method lie in its speed, simplicity and the fact that only ordinary and cheap chemicals are required. It can also be seen in Tables I and II that the method gives a constant positive error of the order of 0.5%.

TABLE I

THE DETERMINATION OF COPPER BY MEANS OF STANNOUS CHLORIDE

Each value is an average of 5 determinations

mg Cu^{+2} by means of $Na_2S_2O_3$	*mg Cu^{+2} by means of $SnCl_2$*	*Difference*	
		mg	*%*
61.64	61.89	+0.25	+0.40
92.47	92.81	+0.34	+0.36
123.29	123.73	+0.44	+0.35
154.11	154.70	+0.59	+0.38
184.93	185.89	+0.96	+0.51
215.75	217.30	+1.55	+0.71

TABLE II

PRECISION OF THE METHOD UNDER THE BEST CONDITIONS

Copper taken 156.97 mg

Expt. No.	*Copper found mg*	*Deviation, d mg*	$d^2 \times 10^4$
1	157.57	+0.061	37.21
2	157.57	+0.061	37.21
3	157.34	—0.169	285.61
4	157.42	—0.089	79.21
5	157.42	—0.089	79.21
6	157.42	—0.089	79.21
7	157.34	—0.169	285.61
8	157.57	+0.061	37.21
9	157.72	+0.211	445.21
10	157.72	+0.211	445.21

Av. $= \overline{x_1} = 157.509$ $\Sigma d^2 = 0.181$

Standard deviation group: $\sigma_{10} = \sqrt{\frac{0.181}{10}} = 0.1346$

Limit of uncertainty of the average $\text{LU}_{\text{av.}} = \overline{x_1} \pm \frac{3\sigma 10}{\sqrt{10}} = 157.381$ to 157.637

Acidity and volume of the solution

The acidity and volume of the solution being titrated play an important part in this titration. Tables III and IV indicate the influence of these factors. An acidity of $0.17N$–$0.68N$ is recommended. Below this acidity, the value found is too low. At higher acidities the end-point is poor and is delayed. Also, near the end-point a premature red-brown colour is produced which disappears rather slowly. However, at higher acidities the reaction appears to be more rapid.

The volume of the solution being titrated has to be maintained between 130 and 200 ml. Unsatisfactory results are obtained if the volume is less than 130 ml, a premature colour change being obtained which takes some time to disappear.

TABLE III

EFFECT OF THE ACIDITY

Cu^{+2} taken: 154.11 mg; volume of the solution at the end of the titration: 150 ml; acid used: hydrochloric acid. Each value is an average of 5 readings.

Normality of acid	*0.1 N $SnCl_2$ ml*	*Cu^{+2} found mg*	*% Recovery*
0.12	23.93	152.74	98.72
0.17	24.36	154.87	100.49
0.34	24.38	154.97	100.59
0.51	24.41	155.19	100.70
0.68	24.40	155.14	100.67
0.85	24.49	155.68	101.02

Titrations in sulphuric acid medium were not good. The end-point is poor, the reaction slow and the initial precipitation of cuprous thiocyanate delayed.

TABLE IV

EFFECT OF THE VOLUME OF SOLUTION BEING TITRATED

Acidity of the solution: 0.34N in hydrochloric acid · copper taken: 156.97 mg. Each value is an average of 5 determinations

Volume of solution at end of titration ml	*0.1 N $SnCl_2$ ml*	*Cu^{+2} found mg*	*% Recovery*
195	24.81	157.72	100.47
170	24.77	157.46	100.31
165	24.75	157.34	100.23
135	24.76	157.40	100.27
120	Not satisfactory		

Titrations with and without passage of carbon dioxide

In technical analyses, it is necessary to simplify the procedure as much as possible. Hence the possibility of avoiding the passing of carbon dioxide through the solution during the titration was investigated. The results are tabulated in Table V. If no carbon dioxide is passed, a slightly higher value is obtained. However, if a pinch of sodium bicarbonate is added just before the titration and if the titration is finished quickly, the value is identical with that obtained when CO_2 is passed through the solution during the titration.

TABLE V

TITRATIONS WITH AND WITHOUT PASSAGE OF CARBON DIOXIDE

Volume of the solution: 150 ml; copper taken: 156.97 mg; acidity of the solution 0.34N

Stream of CO_2 throughout the titration 0.1 N $SnCl_2$ ml	*Titration in air 0.1 N $SnCl_2$ ml*	*Pinch of bicarbonate added just before titration 0.1 N $SnCl_2$ ml*
24.76 (Average of five titrations)	24.79	24.79
	24.75	24.76
	24.81	24.76
	24.82	24.75
	24.81	24.75
	24.84	
	24.87	
	24.79	
	24.82	
	24.85	

SUMMARY

A rapid and simple titrimetric method for the estimation of copper is described. Hydrochloric acid solution of cupric copper is titrated directly with stannous chloride in the presence of thiocyanate using a few drops of 2% ammonium molybdate solution as indicator.

RÉSUMÉ

Une méthode titrimétrique, simple et rapide, est proposée pour le dosage du cuivre. On effectue ce titrage au moyen de chlorure d'étain(II), en présence de thiocyanate de potassium, en utilisant le molybdate d'ammonium comme indicateur.

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ZUSAMMENFASSUNG

Es wird eine einfache, rasche Titrationsmethode zur Bestimmung von Kupfer beschrieben. Das Kupfer wird in Gegenwart vor Thiocyanat und Ammonium-molybdat als Indikator mit einer Zinn(II)-chloridlösung titriert.

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SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM

I. ANTHRANILIC ACID AS A REAGENT

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Anthranilic acid, in weakly acid or neutral solution, combines with copper, cadmium, nickel, cobalt, iron, mercury, lead, zinc, manganese, silver and palladium to form sparingly soluble precipitates, which can either be weighed directly or can be treated with bromate–bromide mixture and determined volumetrically[1].

In this paper the effectiveness of anthranilic acid as a spectrophotometric reagent for osmium is described. In the tetra-, hexa-, and octavalent states and at a pH between 5.5 and 6.5, this metal reacts with anthranilic acid to form a stable dark-violet coloured complex, which shows maximum absorption at 460 mμ. With osmium(IV) the colour develops on heating in less than 10 min, but with osmium(VI) and osmium(VIII) sufficiently stable colour development is attained in the cold after an hour. The colour system obeys Beer's law for osmium(IV) concentrations from 0.5 to 8 p.p.m., the optimum range, against a reagent blank, being 2 to 6 p.p.m., where the % relative error per 1% absolute photometric error is 2.8. The sensitivity of the colour reaction is 1 part of osmium in 125,000,000 parts of solution (Sandell[2]).

The results obtained with the methods of continuous variation[3], molar ratio[4] and slope ratio[5] suggest that with chloro-osmate the reagent forms a 1 : 1 complex, which may be assigned the formula $K[OsCl_4 \cdot C_6H_4NH_2COO^-]$, with an average dissociation constant of $4.6 \cdot 10^{-5}$. The molar ratio method further reveals that at pH 6.0 a portion

of the reagent, is oxidised by osmium tetroxide or by an osmate (OsO_4^{-2}), the reduced osmium(IV) then reacting with the rest of the reagent to form a 1 : 1 complex.

EXPERIMENTAL

Apparatus

All optical density measurements of solutions were made with a Unicam Sp 600 spectrophotometer, Corex glass cells of 1 cm thickness, being used. A Cambridge pH indicator was employed for all pH determinations.

Reagents

Standard osmium solutions. A standard solution of osmium(IV) was prepared by dissolving an accurately weighed quantity of potassium chloro-osmate (K_2OsCl_6), of Johnson and Matthey, in 1 *N* hydrochloric acid.

A 250-ml solution of osmium(VIII) in 0.02 *N* caustic soda solution was prepared from a 0.1 g ampoule of osmic acid (OsO_4), of Dr. Theodor Schuchardt, according to the method of AYRES[6].

For the preparation of a standard solution of osmium(VI), an aliquot of the above stock solution of osmium tetroxide, after reduction by a minimum amount of 1 : 2 alcohol, was made up to a definite volume with distilled water. The solution thus prepared can only be kept for 7 days at an average room temperature of 22°.

Reagent solution. A 2% solution of anthranilic acid (Na salt) was prepared by dissolving 2 g of recrystallised reagent of m.p. 145° in 200 ml water and adding the required amount of sodium carbonate.

Buffer solution. Buffer solution of pH 5.9 was obtained by mixing 9.5 ml of 0.2 *N* sodium acetate with 0.5 ml of 0.2 *N* acetic acid.

Other reagents. Test solutions of palladium(II), ruthenium(III) and rhodium(III) were prepared by dissolving their pure chlorides in dilute hydrochloric acid. The solution of platinum(IV) was obtained by dissolving pure platinum wire in aqua regia and removing the nitric acid from the solution by repeated evaporation with hydrochloric acid. The solution of iridium(IV) was prepared by fusing iridium sponge with a mixture of sodium carbonate and sodium peroxide in a nickel crucible, extracting the product with hot water and acidifying with hydrochloric acid. This solution contained nickel as an impurity.

All other metal solutions were obtained by dissolving analytical grade chlorides, sulphates, nitrates or oxides in water or hydrochloric acid.

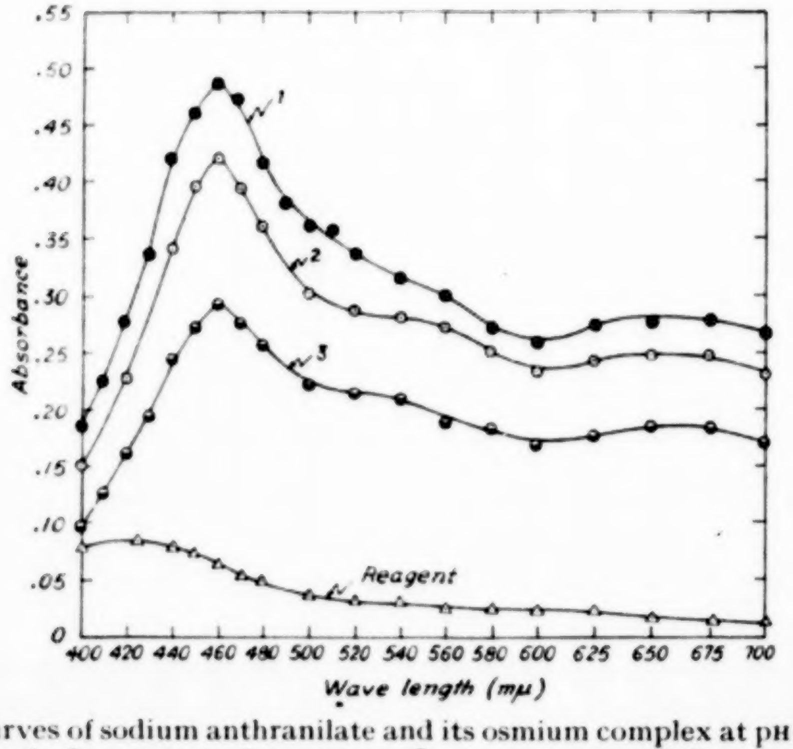

Fig. 1. Absorption curves of sodium anthranilate and its osmium complex at pH 6. Curve 1: 4 p.p.m osmium(IV) + 5 ml of 2% reagent. Curve 2: 3.98 p.p.m. osmium(VI) + 5 ml of 2% reagent. Curve 3: 3.18 p.p.m. osmium(VIII) + 5 ml of 2% reagent.

Absorbance curves

For osmium(IV), an aliquot of potassium chloro-osmate solution was put into a 30-ml beaker and mixed with 5 ml of the reagent solution. After adjusting the pH to 6.0 with dilute sodium hydroxide, the solution was heated on the water bath for 10 min. Then it was allowed to cool to room temperature and afterwards transferred to a 25-ml flask, the solution being made up to volume with distilled water. In the case of osmium(VI) and osmium(VIII), the colour was developed by adding osmate or osmium tetroxide solution to 5 ml of the reagent solution in a 25-ml flask and making up to volume with the buffer solution. The reagent blanks for each valence state were prepared in exactly the same way as the coloured products, omitting the osmium.

The absorption curves of the coloured products obtained from osmium(IV), osmium(VI) and osmium(VIII), measured against reagent blanks, are represented in Fig. 1 together with that of the same amount of the reagent against water at the same pH. In all three cases the colour and its intensity are the same at a pH of about 6.0, and the absorbance curves obtained are superposable, the maxima always being at 460 mμ. The only difference observed was that for full colour development osmium(VI) and osmium(VIII) required, respectively, three and five times as much reagent as osmium(IV).

Effect of pH, reagent and time

It was found that the absorbance of the colour system formed with an excess of reagent increased with increasing pH up to 5.5; from pH 5.5 to 6.5 the absorbance remained constant and then decreased on further increase of the pH. Therefore all subsequent measurements were carried out at pH 5.5 to 6.5

3 ml of the reagent solution was required for maximum development of the colour in the case of 1 to 8 p.p.m. of osmium. Addition of more reagent, up to 5 ml, had no adverse effect on the density of the colour as long as the measurements were made against a reagent blank.

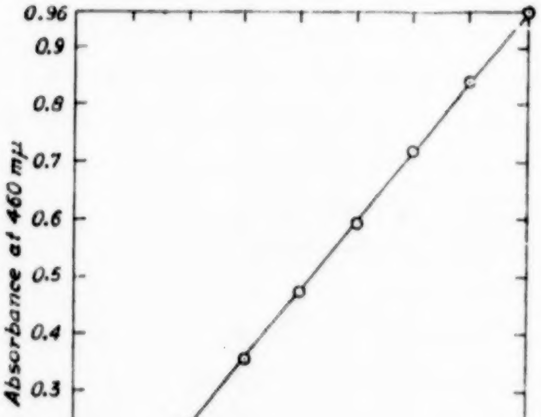

Fig. 2. Beer's law plot for the osmium(IV) complex at pH 6.

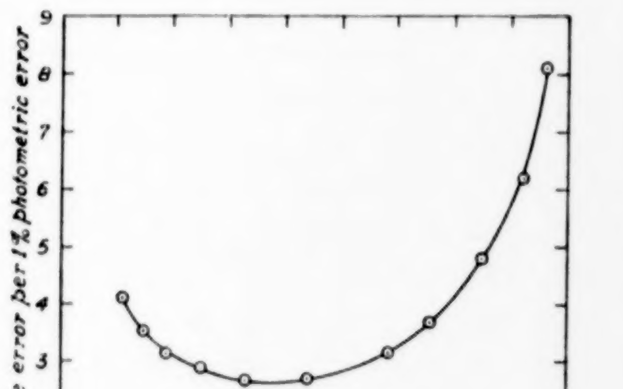

Fig. 3. Evaluation of % relative error ($dc/c \times 100$) relative to 1% absolute photometric error.

Osmium(IV) reacted very slowly with the reagent in the cold, but at the optimum pH and with optimum reagent concentration, the maximum colour was found to develop in less than 10 min when the solution was heated on the water bath. Once developed the colour intensity remained the same for a period of 24 h. The rate of colour development with osmium(VI) and osmium(VIII) was rapid even in the cold and a sufficiently stable colour developed in 1 hour. The colour thus formed was found to maintain its density for 4 hours. When the solution was kept overnight only a very slight increase in the absorbance reading was recorded.

Beer's law, optimum range and accuracy

That the organo-osmium complex obeys Beer's law in the range 0.5 to 8 p.p.m. of osmium(IV) is evident from the straight line obtained on plotting the absorbances against the concentrations (Fig. 2).

Using AYRES equation[7] the % relative error $\left(\frac{dc}{c} \times 100\right)$ per 1% absolute photometric error was calculated and plotted against transmittancy to show how the analytical error varies with the transmittancy (Fig. 3).

To evaluate optimum range and analytical accuracy, RINGBOM's[8] curve was drawn by plotting % absorbancy at 460 mμ as the ordinate and log concentration as the abscissa. Since the accuracy is highest where the curve has the steepest slope, the optimum concentration range (Fig. 4) is between 2 and 6 p.p.m. of osmium. On evaluating the accuracy in this range according to AYRES method[7], a relative analytical error of 2.8% per 1% absolute photometric error was obtained. This is very close to the theoretical value of maximum attainable accuracy (2.72% relative error per 1% absolute error) imposed by Beer's law.

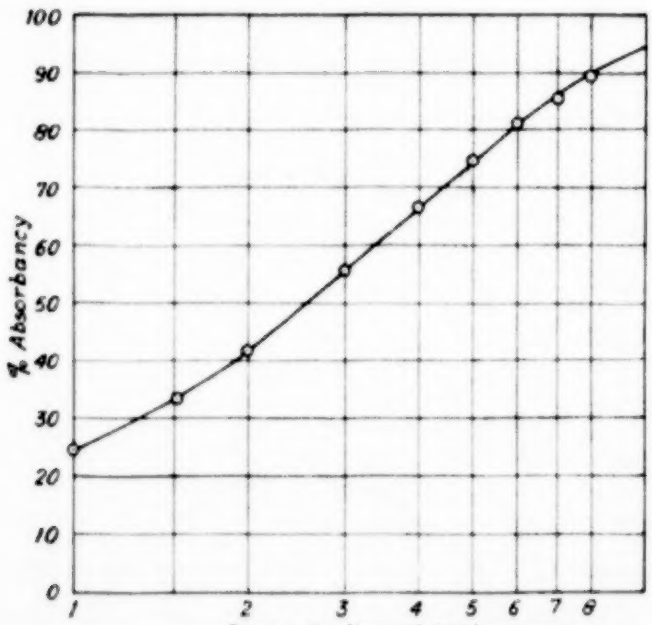

Fig. 4. Calibration curve for the osmium(IV) complex at 460 mμ; pH 6.

Sensitivity

Employing SANDELL's[2] expression for sensitivity, the spectrophotometric sensitivity, as calculated from the Beer's law curve, is given by 0.008 μg/cm^2. This corresponds to a sensitivity of 1 part of osmium per 125,000,000 parts of solution.

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Effect of diverse ions

In order to study the effect of diverse ions solutions were prepared, following the same method as described above, with 3.336 p.p.m. of osmium(IV), varying concentrations of each ionic species to be examined and 0.5 ml of 1% ethylenediaminetetraacetic acid (EDTA) (disodium salt) solution, which was the maximum amount that could be tolerated by the amount of osmium(IV). A difference of more than 0.005 absorbance unit was arbitrarily taken as an interference (*cf.* Table I). In the absence of EDTA, however, most of the common ions and the platinum metals interfered, either by forming a precipitate or a coloured product with the reagent. EDTA (disodium salt) behaves in the same way towards the colour reaction of osmium tetroxide, as it does in the case of osmium(IV) but it considerably reduces the capacity of osmate to form complexes. The presence of tartrate and potassium cyanide should be avoided as they themselves considerably diminish the colour of the complex. Salts of copper, cadmium, aluminium, thorium, zirconium, antimony,

TABLE I

Ions	*Maximum amount of ion tolerated p.p.m.*	*Ions*	*Maximum amount of ion tolerated p.p.m.*
Ru^{+3}	2.252	Mg^{+2}	400
Rh^{+3}	8.18	Ca^{+2}	400
Pd^{+2}	18.6	Sr^{+2}	400
Ir^{+4}	13	Ba^{+2}	100
Mn^{+2}	20	Zn^{+2}	40
Cr^{+3}	15	As^{+3}	200
Fe^{+3}	10	VO_3^-	76
Co^{+2}	20	WO_4^{-2}	52
Ni^{+2}	20	UO_2^{+2}	34
Hg^{+2}	40		

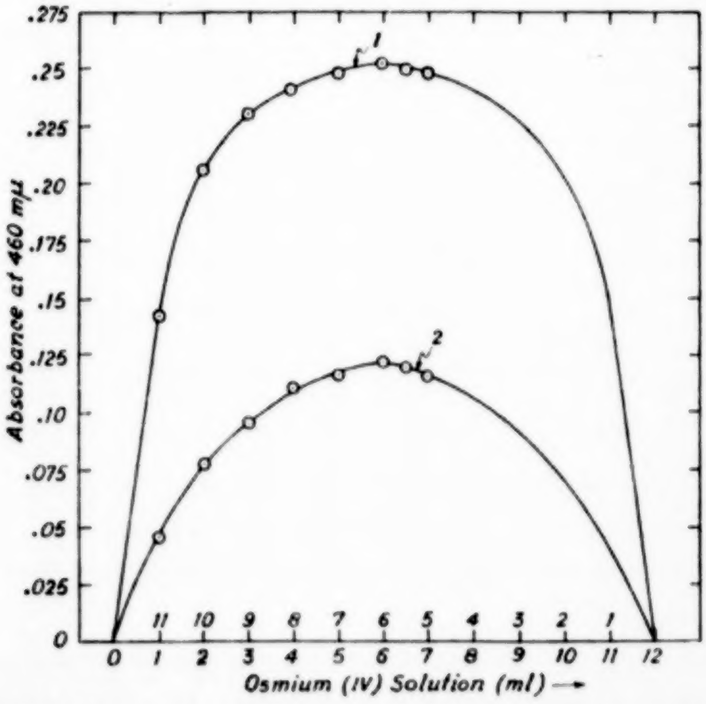

Fig. 5. Determination of the ratio of reagent to osmium(IV) by Job's method. Curve 1: Concn. of osmium(IV) = concn. of anthranilic acid = $25.14 \cdot 10^{-5}M$. Curve 2: Concn. of osmium(IV) = concn. of anthranilic acid = $13.14 \cdot 10^{-5}M$. Total volume in each case 12 ml.

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bismuth and the rare earths must be absent. Gold and platinum interfere as the former precipitates in the metallic state and the latter produces a colour effect.

Composition of the complex in solution

(1) The curves in Fig. 5 were obtained by the application of JOB's method[3] of continuous variation. The peaks of the curves obtained on plotting optical density against increasing amounts of potassium chloro-osmate solution indicate a reagent to osmium(IV) ratio of 1 : 1.

(2) For the molar ratio method[4], solutions were prepared, at pH 6, so that the osmium(IV) concentration remained constant but the ratio of the moles of reagent to the moles of osmium varied from 0.7 to 4. The absorbances of these solutions were measured at 460 mμ against a water blank. The curve in Fig. 6 shows a sharp break at the molar ratio of 1 : 1.

(3) In order to apply the slope ratio method[5] two series of solutions were prepared. One series contained 10 p.p.m. of osmium(IV) as the constant component with varying amounts of the reagent and in the other series the quantities of the reagent and osmium were reversed. The absorbances of the solutions, diluted to 25 ml, were measured at 460 mμ, against a water blank for the first series and a reagent blank for the second. From the results shown in Fig. 7, the slopes of curve 1 (reagent excess) and curve 2 (osmium excess) were calculated to be 0.40 and 0.41, respectively, indicating an osmium to reagent ratio of 1 : 1.

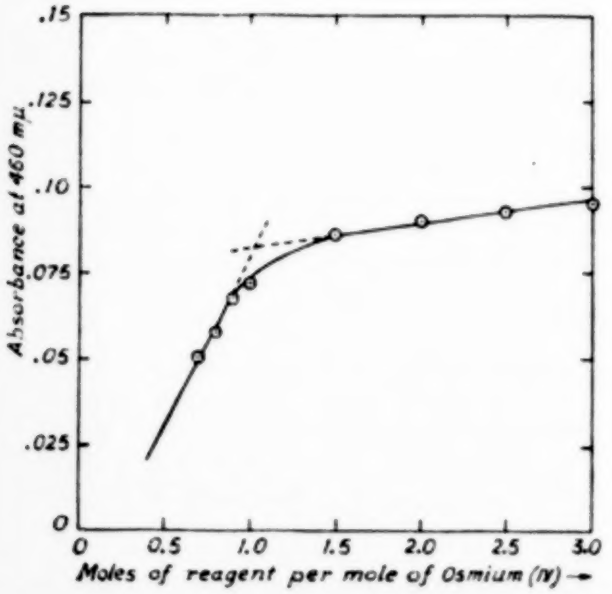

Fig. 6. Determination of the ratio of reagent to osmium(IV) by the molar ratio method.

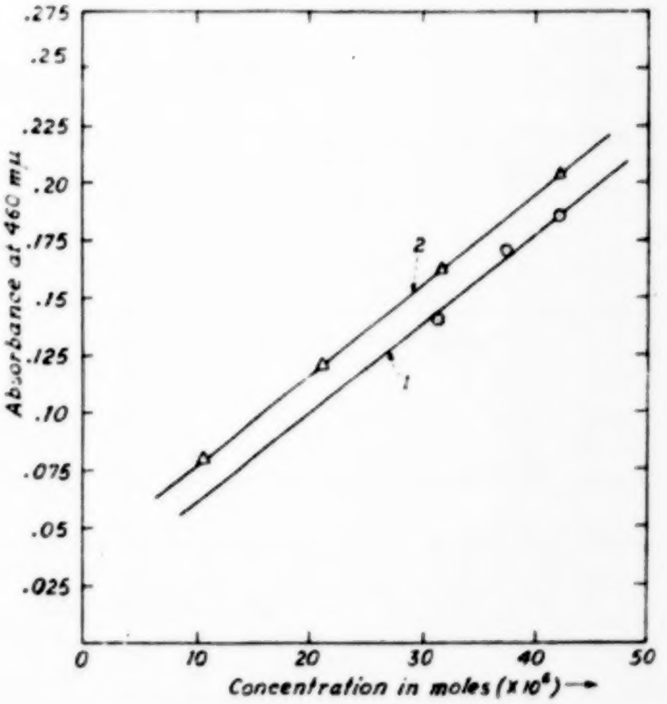

Fig. 7. Determination of the ratio of reagent to osmium(IV) by the slope ratio method.

The results obtained with these three methods prove conclusively that in solution osmium(IV) forms a 1 : 1 complex with the reagent. However, difficulties were encountered when excess of osmium and smaller amounts of reagent were present, because in those cases black osmium dioxide together with metallic osmium were

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precipitated when the pH of the solution increased on the addition of buffer solution. Optical densities of such solutions were, therefore, not measured.

In order to investigate the reaction ratios between osmium tetroxide and the reagent on the one hand and osmate (OsO_4^{-2}) and the reagent on the other by the molar ratio method, solutions were prepared in a 25-ml flask so that the osmium concentration remained constant but the ratio of the moles of reagent to the moles of osmium varied from 0.8 to 6. After the development of the colour by the addition of a drop of 6*M* sulphuric acid, the volume of each solution was made up with the buffer solution. The solutions were allowed to stand for about 2 h before the density against a water blank was measured at 460 mμ (Fig. 8). Curve 1, for osmium tetroxide, and 2, for osmate, show that breaks occur at the points where the ratios between the metal and the reagent are 1 : 5 and 1 : 3, respectively. Since the colour, pH effect, and the wave length of maximum absorption (Fig. 1) of the complex obtained by mixing the reagent with osmium tetroxide or osmate, are the same as those of osmium(IV), it is inferred that most probably the amino groups of the reagent are first oxidised by osmium tetroxide or osmate and that then the reduced osmium(IV) in each case forms a 1 : 1 complex with the excess unoxidised reagent. Thus osmium tetroxide and osmate oxidise, respectively, four and two amino groups of four and two molecules of the reagent and at the same time lose two and one oxygen atoms, respectively.

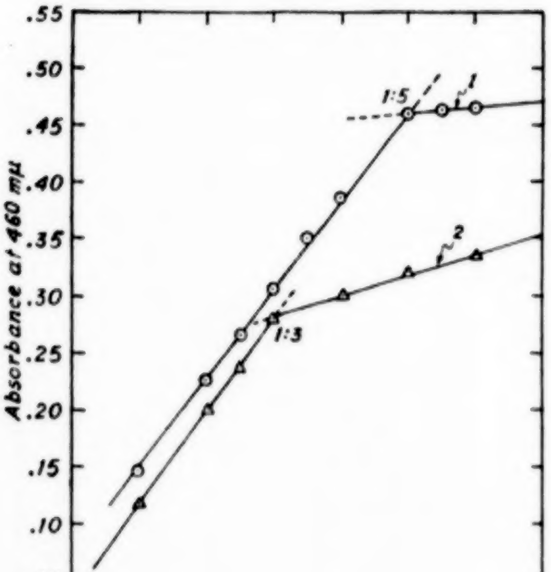

Fig. 8. Determination of the reaction ratios of reagent to (1) osmium(VIII) and (2) osmium(VI) by the molar ratio method.

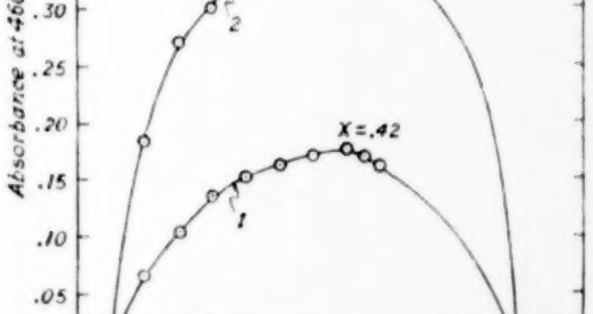

Fig. 9. Absorbance of mixtures of non-equimolecular solutions. Curve 1: $13.14 \cdot 10^{-5}M$ osmium(IV); $26.28 \cdot 10^{-5}M$ sodium anthranilate. Curve 2: $25.14 \cdot 10^{-5}M$ osmium(IV); $75.42 \cdot 10^{-5}M$ sodium anthranilate.

Dissociation constant

From the absorption data (Fig. 9) of the mixtures, at a pH of about 6.0, of non-equimolecular solutions of potassium chloro-osmate and the reagent, the dissociation constant, K, has been evaluated according to the equation reported previously by one of us[9].

Since the values of m and n are 1, the dissociation constant, K, is obtained by substituting in the equation the values of X, p and c given in Table II.

TABLE II

Fig.	*Curve*	*Concn. of Os(IV) $M \cdot 10^5$*	*Concn. of anthranilic acid $M \cdot 10^5$*	X	p	$K \cdot 10^5$
9	2	25.14	75.42	0.42	3	3.6
9	1	13.14	26.28	0.42	2	5.6

Mean: $K = 4.6 \cdot 10^{-5}$.

SUMMARY

Anthranilic acid has been found to be a highly sensitive reagent for the spectrophotometric determination of osmium(IV), osmium(VI) and osmium(VIII) at pH 6.0. In all three valence states the metal reacts with the reagent to form a dark-violet coloured compound, which shows maximum absorbance at 460 mμ. Osmium(IV) can be determined in the presence of diverse ions, if EDTA (disodium salt) is used as a masking agent. The optimum concentration range for the method is 2 to 6 p.p.m. of osmium(IV), where the % relative error per 1% absolute photometric error is only 2.8. By applying JOB's method of continuous variation, the molar ratio method and the slope ratio method, it was established that a 1 : 1 complex is formed between osmium(IV) and the reagent. The reaction of the reagent with osmium tetroxide or osmate indicates that the reagent is first oxidised and that then the reduced osmium(IV) forms a 1 : 1 complex with unoxidised excess reagent. The complex is stable in water and alcohol and has an average dissociation constant of $4.6 \cdot 10^{-5}$.

RÉSUMÉ

L'acide anthranilique est proposé comme réactif sensible pour le dosage spectrophotométrique de l'osmium. Ce dernier peut être dosé en présence de nombreux autres ions, en utilisant l'acide éthylènediaminotétraacétique comme réactif de masquage.

ZUSAMMENFASSUNG

Als empfindliches Reagenz zur spektrophotometrischen Bestimmung von Osmium wird Anthranilsäure vorgeschlagen. Die Gegenwart zahlreicher anderer Ionen stört nicht, sofern sich diese mit Aethylendiaminotetraessigsäure maskieren lassen.

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THE DETECTION AND ESTIMATION OF THIOLSULPHINATES AND THIOLSULPHONATES

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Only recently, in the course of work on the autoxidation of mixtures of olefins and disulphides, has the importance of thiolsulphinates (I) as retarders of free radical chain reactions been recognised[1,2]. It became necessary during this investigation to detect, often in complex mixtures, trace amounts of the latter together with thiolsulphonates (II) as products of their decomposition and further oxidation.

Methods of analysis of these compounds appear to have been only scantily investigated and this paper concerns the development, firstly, of a semi-quantitative paper-chromatographic technique for their detection and, secondly, of methods of functional group analysis by which the purity of larger samples may be accurately measured.

$$R\cdot SO\cdot S\cdot R' \quad (I) \qquad\qquad R\cdot SO_2\cdot S\cdot R' \quad (II)$$

I. CHROMATOGRAPHIC SEPARATION AND DETECTION

Attempts to use untreated paper and conventional solvent systems were unsuccessful giving R_F values of approximately unity both for disulphides and derivatives (I) and (II). Treatment of the paper with phenoxyethanol followed by development with *n*-heptane[3,4] gave well defined spots of useful R_F values and enabled not only thiolsulphinates to be separated from similarly substituted thiolsulphonates but different members of either series to be resolved. Other components of oxidation mixtures did not interfere, olefins and disulphides having high, and olefin hydroperoxide low, R_F values respectively.

Experimental

The chromatographic procedure was exactly as described by LYNN, STEELE AND STAPLE[4] except that Whatman No. 1 filter paper was used and the materials were applied in chloroform solution (loadings up to 60 μg). After development (6–16 h) well defined, almost round spots of 1–2 cm diameter were obtained. Because of unavoidable variations in the amount of phenoxyethanol absorbed on the paper, absolute R_F values were not reliable and either I or II, (R = R′ = Ph), as appropriate, was used as an internal standard. In Table I R_Φ is defined as: distance travelled by sample/distance travelled by standard. These relative values were reproducible to ± 0.03 for thiolsulphinates and ± 0.01 for thiolsulphonates, even when different batches of paper or widely different times of development were used, provided care was taken to get a uniform distribution of phenoxyethanol on the paper. In this respect vertical draining of the paper after soaking in the acetone–phenoxyethanol solution was found more satisfactory than blotting off the excess as originally recommended.

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Location of the spots on the air-dried paper

A. Thiolsulphinates. Two methods have been found equally satisfactory and the choice would depend on the other materials present.

(1) Exposure to hydrochloric acid fumes, with a contact time of 10 sec, is followed immediately by a starch–iodide spray to give a blue-violet spot on a white background with a sensitivity of better than 5 μg/cm^2. Thiolsulphonates and certain sulphoxides give similar spots more slowly and with greatly decreased sensitivity. Acyl peroxides and hydroperoxides also give positive results but are not detected by procedure (2).

(2) The paper is exposed to bromine vapour for 10 sec and sprayed with starch–iodide solution after removal of excess bromine in a rapid stream of air (*ca.* 1–2 min). Blue-violet spots are given by all sulphur compounds which are converted under these conditions to products containing "active" halogen. Aryl and alkyl thiolsulphinates, mono- and di-sulphides can be detected with a sensitivity of 2 μg/cm^2, sulphoxides with a sensitivity of *ca.* 10 μg/cm^2, thiolsulphonates and thiols with a sensitivity of 40 μg/cm^2 and sulphones not at all. The method is similar in principle to the chlorination technique of RYDON AND SMITH[5] for the detection of amino acids and peptides. These, however, do not respond to the milder conditions employed here and negative results were given even by such examples as methionine or cystine which contain mono- and disulphide groups respectively. RYDON AND SMITH similarly found that sulphur-containing amino acids were not detected by their method implying that some interaction between the amino group and halogenated sulphur group is responsible for the failure in both cases. This is confirmed by the work of SCHWARTZ AND PALLANSCH[6] who found, using *tert.*-butyl hypochlorite as the chlorinating agent, that although methionine and other sulphur-containing amino acids again gave negative results, methionine sulphoxide and sulphone, in which S-halogenation is made difficult or impossible, were detected with high sensitivity.

B. Thiolsulphonates. The paper is dipped in a solution of thiophenol in low-boiling petrol (2% v/v), and lightly sprayed, after drying, with bromophenol blue indicator (0.1% solution of sodium salt in water, pH 7). Thiolsulphonates show as distinct yellow spots on a blue background with a sensitivity of better than 5 μg/cm^2. This response is due to the specific reaction of these compounds with thiols to yield sulphinic acids.

$$R\cdot SO_2\cdot S\cdot R' + R''\cdot SH \rightarrow R\cdot SO_2H + R'\cdot S\cdot S\cdot R''$$

Thiolsulphinates also react readily with thiols[7] but give no acidic product and do not interfere even when present in relatively large amounts.

Thiophenol is unpleasant to use and this procedure may be replaced, if desired, by spraying the paper directly with a freshly prepared, aqueous solution of cysteine hydrochloride (5%) and bromophenol blue (0.1%) adjusted to pH 7. The loss in sensitivity under these conditions is slight.

In all the methods of location the size and intensity of the spots are well graduated with respect to the amount of material, which may be estimated semi-quantitatively by visual comparison with a series of standard spots, run on the same sheet of paper, at 5 μg intervals at the lower levels, and containing up to 50 μg of material. Accuracy rapidly diminishes above 40 μg. Spots obtained by a starch–iodide spray are stable for a few minutes only while those due to thiolsulphonates remain unchanged for several hours.

TABLE I

R_Φ VALUES OBTAINED FOR THIOLSULPHINATES AND THIOLSULPHONATES

Thiolsulphinate(I)	R_Φ	*Thiosulphonate(II)*	R_Φ
R = R′ = phenyl	1.0[a]	R = R′ = phenyl	1.0[b]
R = R′ = *p*-tolyl	1.4	R = R′ = *p*-tolyl	1.3
R = R′ = *p*-chlorophenyl	1.3		
R = R′ = *p*-methoxyphenyl	0.25	R = R′ = *p*-methoxyphenyl	0.22
R = phenyl, R′ = *p*-methoxyphenyl	0.60	R = R′ = benzyl	0.60
R = *p*-methoxyphenyl, R′ = phenyl	0.50	R = R′ = ethyl	0.84
R = R′ = ethyl	0.80	R = R′ = *n*-propyl	1.48
R = R′ = *n*-butyl	1.72	R = R′ = *n*-butyl	1.97
$Ph \cdot SO \cdot S \cdot C_6H_4 \cdot O \cdot C_6H_4 \cdot S \cdot SO \cdot Ph$	0.06		

[a] R_F = *ca.* 0.4
[b] R_F = *ca.* 0.3

II. ANALYSIS OF THIOLSULPHINATES AND THIOLSULPHONATES

A. Thiolsulphinates

Unlike sulphoxides, thiolsulphinates could not be quantitatively reduced with titanous chloride. Thus, under the conditions used for saturated sulphoxides[8], results of 60-70% of theory were obtained while reductions in the presence of thiocyanate ion gave improved but variable figures ranging from 85-110% of theory.

The liberation of iodine from iodide ion by thiolsulphinates in the presence of acid has been reported to be quantitative by BRETSCHNEIDER AND KLOTZER[9], and by SCHÖBERL AND GRÄFJE[10]. We have found that, in the presence of mineral acid, decomposition as well as reduction of thiolsulphinates occurs to give results lower than theoretical, while in acetic acid solution the reaction with iodide ion is stoicheiometric only under anaerobic conditions.

Experimental

Materials. Aryl and alkyl thiolsulphinates were prepared by a slight modification of the method of BACKER AND KLOOSTERZIEL[11] and purified by repeated crystallisation or fractional distillation as appropriate. Their physical properties and analytical data are described elsewhere[12].

Recommended procedure. The sample (20–80 mg) is dissolved in acetic acid (15 ml, AnalaR grade) in a small Erlenmeyer flask equipped with a side arm and magnetic stirrer. The solution is outgassed with a stream of carbon dioxide introduced *via* a coarse capillary through the side arm. The capillary is then withdrawn from the solution and washed down with a little oxygen-free acetic acid. A similarly outgassed, saturated, aqueous solution of potassium iodide (2 ml) is added and the mixture stirred for 2 min in the stoppered flask. The liberated iodine is then titrated slowly, and with stirring, under an atmosphere of carbon dioxide, to a starch end-point using standard thiosulphate.

$$\%\ \text{purity} = \frac{\text{Mol. wt. of thiolsulphinate} \times \text{thiosulphate normality} \times \text{titre} \times 100}{2000 \times \text{sample wt.}}$$

Results

The results are summed up in Tables II and III.

TABLE II

ANALYSIS OF PHENYL BENZENETHIOLSULPHINATE

Sample wt. (*g*)	*Thiolsulphate required* (*ml 0.0200N*)	*Found* (*% of theory*)	*Mean*	*Standard deviation*
0.0516	21.75	98.7	99.3	0.45
0.0522	22.15	99.3		
0.0500	21.30	99.7		
0.0504	21.40	99.4		
0.0486	20.50	98.8		
0.0501	21.35	99.8		

TABLE III

ANALYSIS OF OTHER THIOLSULPHINATES (I)

(*I*)	*Found* (*% of theory*)	*Standard deviation*
R = R′ = *p*-methoxyphenyl	98.4	0.30
R = R′ = ethyl	96.6	0.52
R = R′ = *n*-butyl	95.7	0.33
$Ph \cdot SO \cdot S \cdot C_6H_4 \cdot O \cdot C_6H_4 \cdot S \cdot SO \cdot Ph$	94.7	0.34

Discussion

Oxygen-free conditions were found necessary to prevent an induced oxidation of iodide which otherwise led to results higher than the theoretical by 2-3% and a lower precision. Thus 5 replicate analyses in air of the sample of phenyl benzenethiolsulphinate used for the results in Table II gave a mean value of 102.7% of theory with a standard deviation of 1.35.

The sample size could be varied between wide limits provided a concentration of 80 mg/15 ml solvent was not exceeded. As shown in Table IV higher concentrations led to correspondingly lower results for reasons which are not completely understood.

As thiolsulphonates are the most likely impurity associated with thiolsulphinates it was of importance to examine any interference they might cause. Alone they liberated iodine, under the recommended conditions, equivalent to *ca.* 25% of theory (based on complete reduction of the $>SO_2$ group) while in the presence of thiolsulphinate their reduction was further suppressed to less than half of this figure. Thus, as shown in Table V, for a mixture of thiolsulphinate and thiolsulphonate the found values for the former were higher than the calculated values by only a fraction of the thiolsulphonate content.

The chromatographic procedure detailed earlier may be conveniently used to confirm the presence or absence of thiolsulphonate in thiolsulphinate.

(*B*) *Thiolsulphonates*

The reaction of thiolsulphonates with thiols has been investigated by several workers[13-16] mainly in respect of the identity of the products. It has now been shown that, under the proper conditions, the yield of sulphinic acid is stoicheiometric and may be used to estimate, as well as to detect, thiolsulphonates.

Experimental

Materials. Aryl thiolsulphonates were obtained by the spontaneous decomposition of the appropriate sulphinic acids[17]. Chlorination of disulphides in acetic acid solution containing water (4 mole/mole disulphide) gave alkyl thiolsulphonates as the major product in contrast to the results of LEE AND DOUGHERTY[18]. Benzyl disulphide was oxidised directly to the corresponding thiolsulphonate as described by HINSBERG[19]. Solid products were crystallised to constant melting point from petrol–chloroform; liquids were repeatedly distilled in high vacuum. Fractional elution from silica gel with carbon tetrachloride–chloroform was used in certain cases for final purification.

Recommended method

A. The sample (1 mmole) is dissolved in acid free ethanol (5 ml) and a solution of thiophenol in ethanol (2 ml, 20% v/v) added with swirling. The resulting sulphinic acid is titrated with 0.1*N* sodium hydroxide to the first blue colour of bromophenol blue as indicator. The end-point is sharp and the indicator blank less than one drop of titrant.

Smaller samples (0.1-0.2 mmole) may be similarly analysed by reducing the volume of thiophenol solution to 1 ml and the strength of the sodium hydroxide to 0.02*N*. The indicator blank is proportionately larger and it is advisable to perform such a blank first and to match the end-point of subsequent titrations to the end-point colour of the blank. The accuracy and precision of analyses of aryl thiolsulphonates on this smaller scale is unaltered but in the case of alkyl derivatives the results tend to be slightly lower (*ca.* 1%) than on the full scale, with a lower precision also (standard deviation *ca.* 2).

$$\%\ \text{purity} = \frac{\text{titre} \times \text{normality of alkali} \times \text{mol.wt. of thiolsulphonate} \times 100}{1000 \times \text{sample weight}}$$

B. Where the sample is dissolved in a water-immiscible solvent the unfavourable partition properties of the sulphinic acid make direct titration with aqueous alkali difficult. An aliquot of the sample containing 0.5–1 mmole is dissolved in acid-free chloroform (2 ml) and a solution of thiophenol in chloroform (2 ml, 20% v/v) added with swirling followed by an excess (15–20 ml) of 0.1*N* sodium hydroxide solution. After a vigorous shaking the alkali remaining is then titrated with 0.1*N* hydrochloric acid using bromophenol blue as indicator. The end-point is taken as the blue-grey transition colour of the indicator and, with care, may be judged to within one drop of titrant. A blank analysis is performed omitting only the thiolsulphonate.

$$\%\ \text{purity} = \frac{(\text{Blank-titre}) \times \text{normality of acid} \times \text{mol.wt. of thiolsulphonate} \times 100}{1000 \times \text{sample weight}}$$

TABLE IV

INFLUENCE OF SAMPLE SIZE ON ACCURACY OF ESTIMATION OF PHENYL BENZENETHIOLSULPHINATE

Sample wt. (g) in 15 ml solvent	*Found (% of theory)*
0.0504	99.4
0.0666	98.8
0.0790	98.5
0.1116	97.0
0.1358	96.4
0.2005	91.2
0.2015[a]	98.7

[a] Dissolved in 30 ml acetic acid

TABLE V

INTERFERENCE BY THIOLSULPHONATE IN ANALYSIS OF THIOLSULPHINATE

Composition of mixture		*Thiolsulphinate found % w/w)*
Phenyl benzenethiolsulphinate (% w/w)	*Phenyl benzenethiolsulphonate (% w/w)*	
87.6	12.4	88.8
81.0	19.0	84.9
49.0	51.0	59.4
0.0	100.0	44.0

TABLE VI

PHYSICAL CONSTANTS OF THIOLSULPHONATES

Structure	*M.p.*	*B.p.*	n_D^{20}	*Found*	*Required*
R = R′ = phenyl	37.5—38.5°	—	—	C, 57.5; H, 4.0; S, 25.6	C, 57.6; H, 4.0; S, 25.6
R = R′ = ethyl	—	70°/0.02 mm	1.4988	C, 31.4; H, 6.5; S, 41.4	C, 31.2; H, 6.5; S, 41.6
R = R′ = benzyl	103—105°	—	—	C, 60.6; H, 5.1; S, 23.3	C, 60.4; H, 5.0; S, 23.0
R = R′ = *n*-propyl	—	79°/0.03 mm	1.4924	C, 39.7; H, 7.9; S, 34.9	C, 39.5; H, 7.7; S, 35.2
R = R′ = *n*-butyl	—	103°/0.05 mm	1.4873	C, 45.9; H, 8.6; S, 30.5	C, 45.7, H, 8.6; S, 30.5
R = R′ = *p*-methoxyphenyl	87—8°	—	—	C, 54.5; H, 4.5; S, 20.5	C, 54.2; H, 4.5; S, 20.6

Results

See Tables VII and VIII.

TABLE VII

ANALYSIS OF PHENYL BENZENETHIOLSULPHONATE

Method	*Sample wt* (g)	*Found* (% of theory)	*Mean*	*Standard deviation*
A	0.0500	99.7	99.8	0.46
A	0.0506	100.7		
A	0.0505	99.4		
A	0.0513	99.9		
A	0.0505	99.3		
A	0.1452	99.9		
A	0.2149	99.6		
B	0.0484	100.9	99.4	1.02
B	0.0750	100.0		
B	0.1259	98.4		
B	0.1481	99.6		
B	0.1842	98.4		
B	0.2241	98.9		
B	0.2490	100.4		
B	0.2954	98.2		

TABLE VIII

ANALYSIS OF OTHER THIOLSULPHONATES

Structure (II)	*Method*	*Found* (% of theory)	*Standard deviation*
R = R′ = ethyl	A	99.1	0.11
R = R′ = ethyl	B	100.4	1.08
R = R′ = *n*-propyl	A	99.0	0.18
R = R′ = *n*-butyl	B	96.5	0.51
R = R′ = benzyl	B	98.5	0.15
R = R′ = *p*-methoxyphenyl	B	96.7	0.68

Discussion

The reaction between thiolsulphonates and thiols is practically instantaneous at room temperature. There appears to be no restriction on sample size from 0.1 mmole upwards provided that excess thiol is present and that suitable adjustments are made in the strengths of alkali and acid used.

In the direct titration of a sulphinic acid in the presence of thiophenol it can be calculated by standard methods that the equivalence point under the given experimental conditions will be reached at pH 4.2–4.4 taking the pK_A values for thiophenol[20] and a sulphinic acid[21] as 7.8 and *ca.* 1.5 respectively. Of the indicators whose transition period includes this pH range bromophenol blue was found to be the most useful. No screened indicator tried was suitable.

No interference by impurities, other than those which are acidic to the indicator, has been encountered. Thus thiolsulphinates, even when present in large amounts, do not affect the estimation although they react equally readily with thiols[7].

$$\mathrm{R \cdot SO \cdot S \cdot R' + R'' \cdot SH \rightarrow [R \cdot SOH] + R' \cdot S \cdot S \cdot R''}$$

$$\mathrm{[R \cdot SOH] + R'' \cdot SH \rightarrow R \cdot S \cdot S \cdot R'' + H_2O}$$

TABLE IX

ESTIMATION OF PHENYL BENZENETHIOLSULPHONATE IN THE PRESENCE OF PHENYL BENZENETHIOLSULPHINATE

Thiolsulphonate	*Thiolsulphinate*	*Thiolsulphonate found* (% *of theory*)
0.0494	0.2265	98.7
0.3165	0.1778	98.7

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SUMMARY

Procedures are described for the separation and detection of thiolsulphinates and thiolsulphonates on paper chromatograms, together with methods for the estimation of these substances.

RÉSUMÉ

Des méthodes chromatographiques sont proposées pour la détection et la séparation des thiosulfinates et des thiosulfonates, ainsi que des méthodes pour le dosage de ces substances.

ZUSAMMENFASSUNG

Es wird ein papier-chromatisches Verfahren beschrieben zur Trennung und zum Nachweis von Thiosulfinaten und Thiosulfonaten, sowie Methoden zur deren Bestimmung angegeben.

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A SEMIMICRO METHOD FOR THE DETERMINATION OF FLUORINE AND PHOSPHORUS IN ORGANIC COMPOUNDS CONTAINING BOTH THESE ELEMENTS

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In the course of the development of an analytical method for the determination of fluorine in organic compounds[1], we were confronted with the need for extending this method to organic fluoro compounds containing also phosphorus. Our original method was based on the oxidative combustion of the sample with sodium peroxide in an electrical ignition bomb of the Parr type, and determination of the fluoride ion formed by titration with thorium nitrate solution and alizarinsulfonate as indicator. The method is affected by even very small quantities of phosphate ion, which destroys the colored lake. It is therefore necessary to remove the phosphate prior to the determination of the fluoride. Various methods have been proposed, such as distillation of the hydrogen fluoride[2-5], or precipitation of the phosphate ion[6-9]. Some experiments have been carried out to adapt FENNELL's[8] method (separation of the phosphate from the fluoride as silver phosphate) to organic compounds and to a semimicro scale. The melt obtained by combustion was dissolved and percolated through a cation-exchange resin. The effluent was acidified with nitric acid (pH 2), and the solution gently boiled to remove carbon dioxide, and neutralized with $0.1N$ sodium hydroxide. At pH 8.2–8.4 the phosphate was precipitated by vigorously stirring with an excess of $0.1N$ silver nitrate solution. By addition of $0.05N$ sodium hydroxide, the pH was brought to 10.6–10.8 and the yellow-brown precipitate of silver phosphate and silver hydroxide filtered and washed with alkaline water. The combined filtrate and washings were made up to 500 ml and the fluoride was determined in an aliquot of 10 ml as described[1], but using $0.1N$ nitric acid instead of hydrochloric acid. This method gave reasonably good results, when the analysis was carried out without interruptions. Too high values resulted, when the final solution was left standing for several hours.

It seemed worthwhile to separate the two anions by an exchange-resin and thus to make possible their simultaneous determination. While this work was in progress, two similar attempts have been reported[10,11].

EXPERIMENTAL

Reagents

Standard sodium fluoride solution, containing 0.1 mg F/ml; thorium nitrate solution, approximately $0.015N$; sodium alizarin-sulfonate reagent; buffer solution, pH 3.55; sodium peroxide; hydrochloric acid, appr. $0.1N$; ethyl alcohol; sucrose.

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* Part of a thesis submitted by JOSEF LIPKE to the Technion-Israel Institute of Technology in partial fulfillment of the requirements for the degree of Master of Science.

All the above mentioned reagents and solutions were prepared as specified before[1].

Potassium dihydrogen phosphate standard solution; sulfuric acid, appr. 1 N; acetone; molybdate reagent.

These reagents and solutions were prepared according to BERNHARDT AND WREATH[12].

Sodium hydroxide solution 0.25 N and 1 N. The sodium hydroxide used should be of analytical grade and should contain not more than 1% carbonate.

Ion-exchange resins. The cation exchanger Amberlite IR-112 (Rohm and Haas, Philadelphia, Pa., U.S.A.), which is no longer supplied, has been replaced by Dowex-50 X 4, 20–50 mesh (Dow Chemical Co., Midland, Mich., U.S.A.); Amberlite IRA-400 (Rohm and Haas), an anion-exchange resin, 20–50 mesh.

Apparatus

In addition to the 8-ml semimicro electric ignition bomb described previously[1], three types of columns were prepared (Figs. 1, 2, 3). Their interior and tips were covered with paraffin, after a thorough cleaning with chromic acid–sulfuric acid mixture. They contained a perforated plastic disc at the bottom, supporting the resin column, and a small cotton plug in their constricted part, to prevent the resin from being washed out. The columns are provided with interchangeable ground joints and column II with an additional plastic diaphragm burette tap, containing no glass parts (Fig. 4). This valve permits control of the flow in the columns. Columns I and III contain the cation-exchange resin (acidic form), while column II contains the anion-exchange resin (basic form).

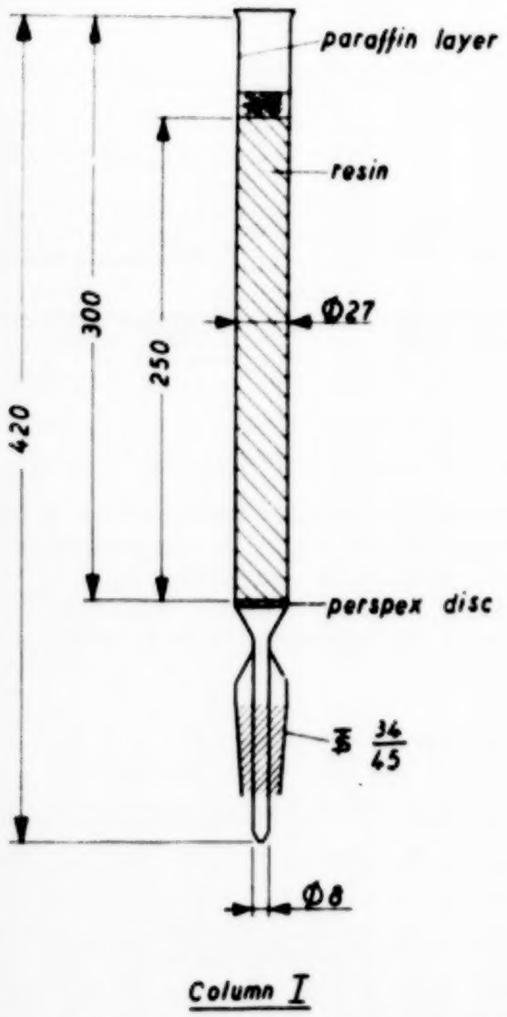

Fig. 1. Column I, containing the cation-exchange resin.

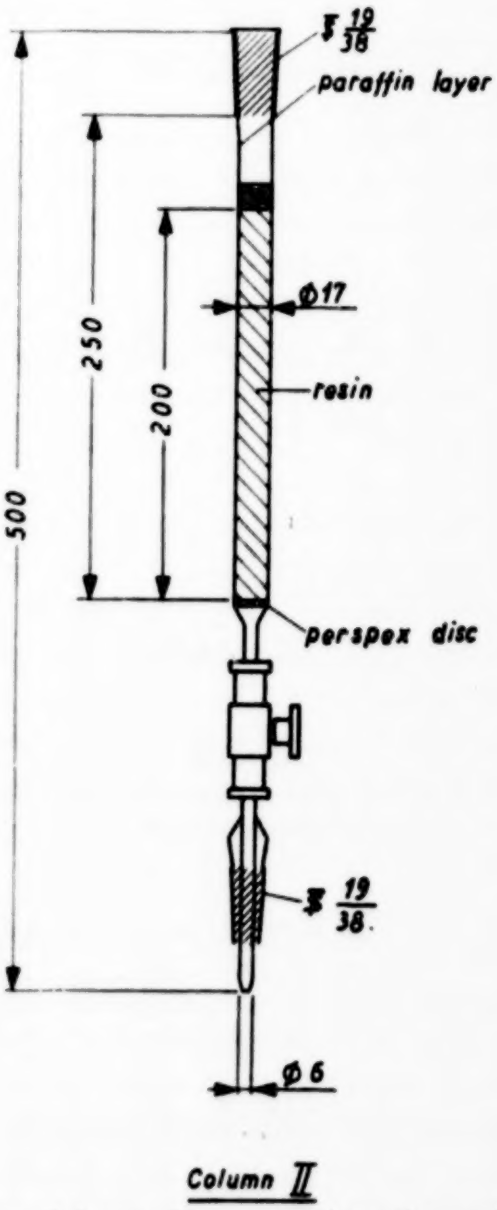

Fig. 2. Column II, containing the anion-exchange resin.

Procedure

The phosphate was determined according to BERNHARDT AND WREATH[12]. We used a Hilger-Spekker absorptiometer H 760, fitted with No. 1 Kodak filters (transmittance 405 to 455 mμ) and 2-cm Corex absorption cells. Calibration (see Table I) is carried out using a potassium dihydrogen phosphate solution in the range of 20 to 120 μg of phosphorus per 3 ml solution. This method gives good results, provided the glassware is scrupulously cleaned and the distilled water used contains no heavy metal ions. Working in a shaded place is recommended, as the molybdate deteriorates in direct sunlight.

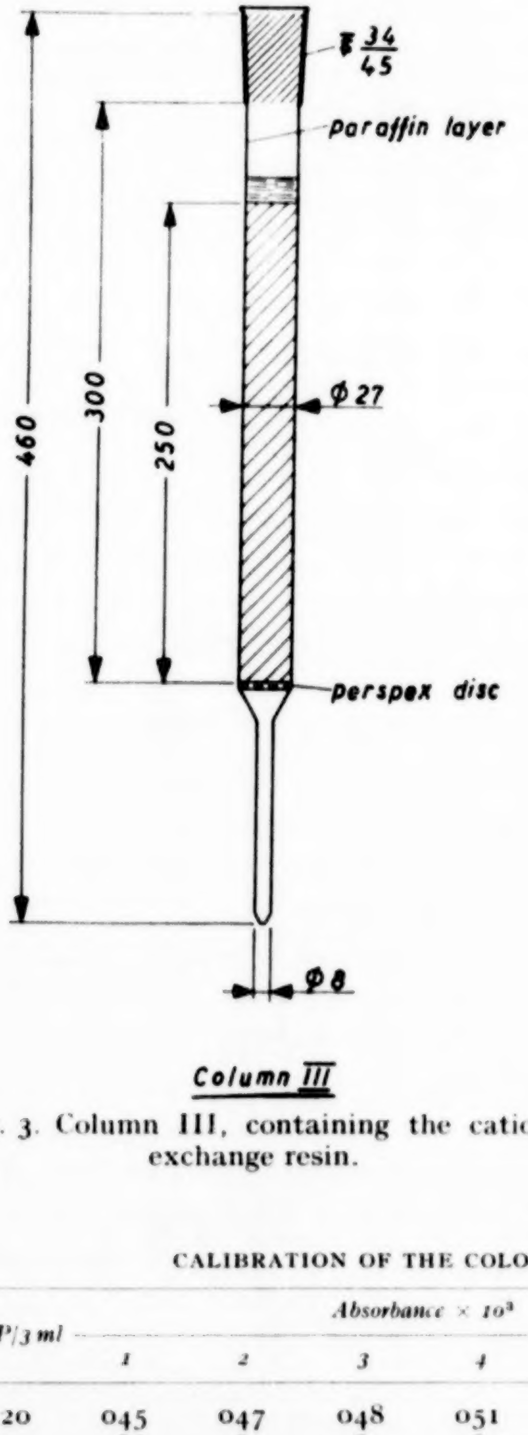

Fig. 3. Column III, containing the cation-exchange resin.

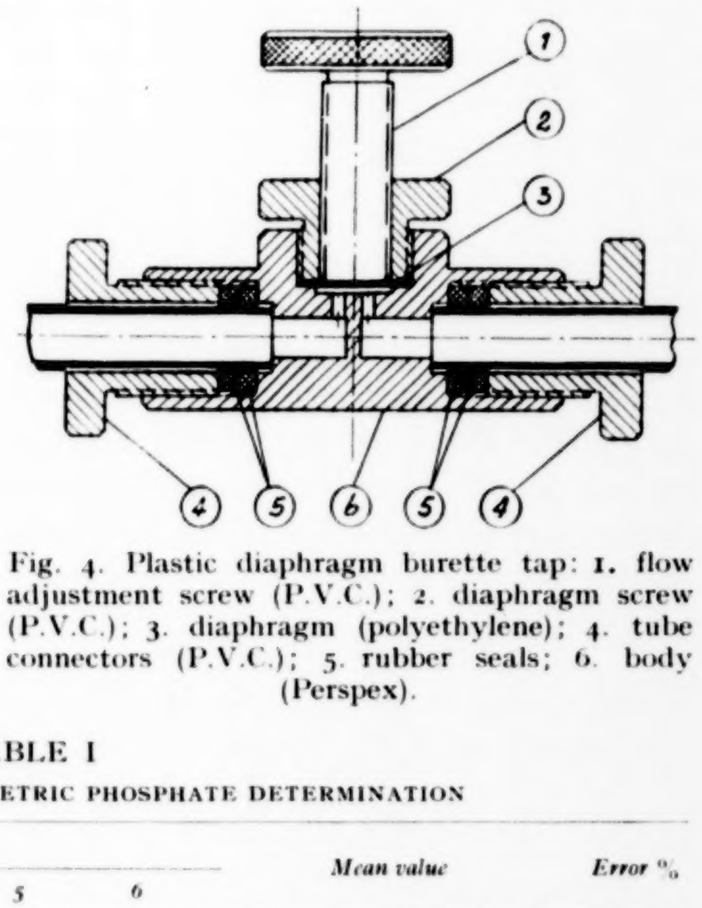

Fig. 4. Plastic diaphragm burette tap: **1.** flow adjustment screw (P.V.C.); 2. diaphragm screw (P.V.C.); 3. diaphragm (polyethylene); 4. tube connectors (P.V.C.); 5. rubber seals; 6. body (Perspex).

TABLE I

CALIBRATION OF THE COLORIMETRIC PHOSPHATE DETERMINATION

μg P/3 ml	*Absorbance × 10^3*						*Mean value*	*Error %*
	1	*2*	*3*	*4*	*5*	*6*		
20	045	047	048	051	045	042	0.046 ± 0.0013	2.8
40	086	083	085	084	087	086	0.085 ± 0.0006	0.7
60	124	123	126	125	126	119	0.124 ± 0.0011	0.9
80	158	159	161	160	161	156	0.159 ± 0.0008	0.5
100	197	196	195	198	191	191	0.195 ± 0.0012	0.6
120	231	230	235	230	228	229	0.231 ± 0.0010	0.4

The fluorine determination was carried out as described before[1].

Preparation of the ion-exchange columns

Pretreatment of the Dowex-50 X 4 resin. 500 g of the resin was washed several times with distilled water, 1*N* sulfuric acid, and 1*N* sodium hydroxide solution, each operation being continued until the supernatant appeared colorless.

Finally, the resin in the acid form was washed thoroughly with distilled water until no more sulfate ions could be detected in the washings.

Preparation of columns I and III. The columns were filled with the pretreated cation exchange resin, as uniformly as possible to prevent channeling, leaving a free space of about 5 cm height at the top of the columns.

Regeneration of columns I and III. After each analysis, columns I and III were connected, and 1 l of 1*N* sulfuric acid solution was passed through them. Each column was washed separately with distilled water until the percolate was free of sulfate ions.

Pretreatment of the Amberlite IRA-400 resin. A quantity of 100 g of the resin was washed several times with distilled water, 1*N* sodium hydroxide solution, and 1*N* hydrochloric acid solution. This sequence is repeated twice and each operation continued until the supernatant appears colorless.

Preparation of column II. The basic form of the pretreated resin is filled as uniformly as possible into the column, leaving again a free space of about 5-cm height at the top. One cycle of treatment was performed in the column and the latter washed with distilled water until the effluent had ± pH 8.

Regeneration of column II. After each analysis, about 800 ml of 1*N* sodium hydroxide solution was passed through the column and the latter washed with distilled water until the effluent showed again pH 8. (In case the phosphate has been eluted from the column in the course of the phosphate determination, only half the volume of the regenerative solution is required.)

Amberlite IRA-400 changes its characteristics while in use, and its capacity diminishes in spite of the regeneration. Its activity should be checked from time to time and when not satisfactory, the filling of column II should be replaced. This check is carried out as follows: a mixture of 0.3 g of sodium monohydrogen phosphate dodecahydrate, 4 g of sodium hydroxide and 1 g of sodium carbonate is dissolved in 80–100 ml of distilled water and steps 1 and 2 are carried out as described below. An aliquot of 10 ml is then titrated with 0.015*N* thorium nitrate solution as usual, and should require only 0.03–0.04 ml. When this value is exceeded, the filling must be discarded.

ANALYTICAL METHOD

Up to 100 mg of the dried and powdered sample is ignited in the Parr sodium peroxide bomb, as described[1], the weight of the sample being chosen so that the final concentration of fluorine be 0.1–0.3 mg/10 ml. The phosphate concentration should be adjusted to the range quoted above by proper dilution. The melt is dissolved in distilled water, transferred to a 100-ml volumetric flask and filled up to the mark. Halogens other than fluoride and sulfur (as sulfate) can be determined independently in aliquots of this solution by standard methods. In contrast to fluorine, which must be separated from the phosphate prior to its determination, the phosphorus (as phosphate) can be determined in aliquots by the described[12] colorimetric method, as fluoride and other halogens, carbonate and sulfate ions do not interfere. Of course it can also be determined in an aliquot of the solution collected after separation of the fluoride ion by continuous elution of the column (step 3).

This last procedure is necessary in case the quantity of the sample available is limited and its fluorine and phosphorus content low.

Separation of fluoride and phosphate

The recommended rate of percolation is 4–5 ml/min. It should be controlled from

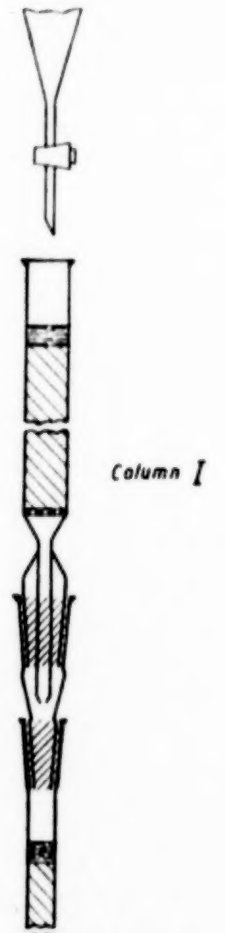

Fig. 5. First step of the analysis: adsorption of cations in column I and anions in column II.

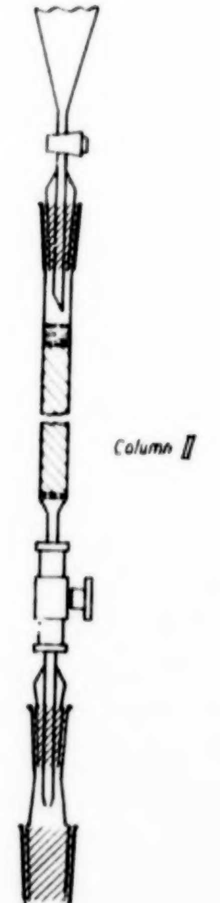

Fig. 6. Second step of the analysis: elution of the fluoride ion and adsorption of the cations of the eluent in column III.

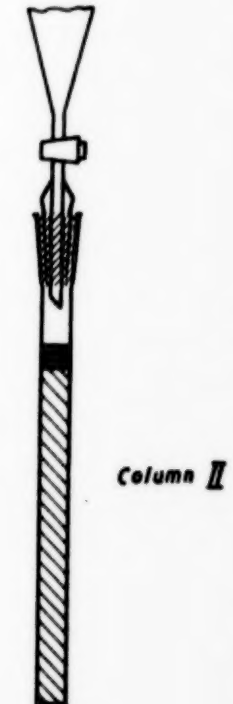

Fig. 7. Third step of the analysis: elution of the phosphate ion.

time to time, as it is dependent on, and proportional to, the liquid height. To ensure good adsorption and avoid channeling, the resins should always be covered with liquid.

First step. The solution is transferred into a separating funnel, attached to the top of both columns I and II (Fig. 5). The solution is percolated and washed down with 300 ml of distilled water; the effluent is discarded. Column I adsorbs the cations, while the anions in the resulting acid solution pass into column II and are adsorbed there.

Second step. Column I is disconnected and replaced by a separating funnel of 500 ml capacity. This and column II are placed on top of column III (Fig. 6), and about 600 ml of 0.25*N* sodium hydroxide is percolated. The first 100 ml of the effluent are discarded and the remaining 500 ml are collected in a 500-ml volumetric flask (alkaline reaction to phenolphtalein is maintained in the flask by addition of 0.25*N* sodium hydroxide solution) and made up to the mark with distilled water. The fluorine content is determined in 10 ml aliquots by the method described[1].

Third step. Column III is disconnected (Fig. 7), 450 ml of 1*N* sodium hydroxide solution passed through column II and the effluent collected in a 500-ml volumetric flask, acidified with approximately 26 ml of conc. sulfuric acid, giving an overall acid concentration of 1*N*, and brought up to the mark with 1*N* sulfuric acid solution. The phosphate content is determined in an aliquot by the colorimetric method[12].

RESULTS AND DISCUSSION

The method described here is based on differential elution of the anion-exchange resin. As the final solution analysed contains in addition to phosphate and fluoride

TABLE II

SEPARATION OF FLUORIDE AND PHOSPHATE IONS IN MIXTURES OF PURE SALTS

Composition of salt mixture		*Found in step 2*	*Found in step 3*
	g	g	g
PO_4^{-3}	0.075	none	—
NaOH	4.0	—	—
Na_2CO_3	1.0	—	—
PO_4^{-3}	0.075	none	—
NaOH	4.0	—	—
Na_2CO_3	1.0	—	—
Cl^-	0.032	—	—
PO_4^{-3}	0.075	none	—
NaOH	4.0	—	—
Na_2CO_3	1.0	—	—
SO_4^{-2}	0.066	—	—
F^-	0.0127	0.01266	—
PO_4^{-3}	0.075	—	0.074
NaOH	4.0	—	—
F^-	0.0127	0.01268	—
PO_4^{-3}	0.075	—	0.076
NaOH	4.0	—	—
Na_2CO_3	1.0	—	—

ions, carbonate from the combustion of the organic matter, sodium hydroxide and in case of the presence of other elements in the sample, their respective ions, the accuracy of the method was proven by the analysis of artificial salt mixtures of approximately the same composition. It was found that the fluoride and the phosphate could be separated and quantitatively recovered and determined with good results. The results are summarized in Table II.

A number of organic phosphorus compounds containing fluorine has been analyzed by this method. The results are summarized in Table III. The mean error in these determinations is about −0.7% for fluorine and − 1.2% for phosphate.

TABLE III

EXAMPLES OF FLUORINE AND PHOSPHORUS DETERMINATIONS IN ORGANIC COMPOUNDS

Compound	*Formula*	*Calculated*		*Found*		*Error*	
		% F	*% P*	*% F*	*% P*	*% F*	*% P*
Diisopropyl fluorophosphate	$C_6H_{14}FO_3P$	10.32	16.82	10.35	16.77	+0.29	−0.3
Diethyl 2-fluoroethyl-phosphate	$C_6H_{14}FO_4P$	9.49	15.48	9.39	15.33	−1.05	−0.97
Methanephosphonic acid difluoride	CH_3F_2OP	37.97	30.98	37.77	30.64	−0.53	−1.1
Diisopropyl 2-fluoroethyl-phosphate	$C_8H_{18}FO_4P$	8.33	13.57	8.27	13.37	−0.7	−1.5
Di-(2-fluoroethyl) benzenephosphonate	$C_{10}H_{13}F_2O_3P$	15.19	12.38	15.05	12.21	−0.9	−1.4
1,1-Di-(*p*-fluorophenyl)-ethylene-2-phosphonic acid	$C_{14}H_{11}F_2O_3P$	12.83	10.46	12.75	10.26	−0.6	−1.9

ACKNOWLEDGEMENT

The authors are indebted to Dr. ERNST D. BERGMANN and Dr. DAVID GINSBURG for their interest in this work and to Dr. ZVI PELCHOWICZ for the preparation of the samples.

SUMMARY

The fluorine and phosphorus in the organic compound are transformed into fluoride and phosphate ions. These ions are adsorbed after percolation of the whole solution through a cation-exchange resin, on a basic resin and eluted fractionally. Bromine, chlorine and sulfur can be determined simultaneously with the fluorine and the phosphorus.

RÉSUMÉ

Une méthode est proposée pour le semimicrodosage du fluor et du phosphore dans les composés organiques. Le fluorure et le phosphate obtenus par fusion au peroxyde de sodium sont traités par des échangeurs d'ions et séparés par élution fractionnée.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Halbmikro-Bestimmung von Fluor und Phosphor in organischen Verbindungen. Die nach dem Aufschluss mit Natrium-peroxyd erhaltenen Fluorid- und Phosphat-Ionen werden an einem Austauscherharz absorbiert und dann selektiv eluiert. Brom, Chlor und Schwefel können mitbestimmt werden.

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PHOTOMETRIC DETERMINATION OF NICKEL IN COPPER-NICKEL ALLOYS

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Nickel may be determined in the presence of copper by the absorptiometric measurements of nickel nitrate solutions at a wavelength of 3900 Å. Precision photometric technique is used and the method has been used from about 1 to 32% nickel in copper-nickel alloys. A single determination can be completed within 5 min.

METHOD

Apparatus

A Beckman Model B spectrophotometer was used with 2 cm tube-cells.

Procedure

Dissolve 1.000 g of alloy in 10 ml of nitric acid (s.g. 1.4) in a 100-ml beaker and boil to remove nitrous fumes (nitrites interfere and boiling is necessary). Remove the beaker from the hot plate, allow to cool to about 80° then add 10 ml of phosphoric acid (1:10). (Manganese, as permanganate will interfere if phosphoric acid is added before boiling ceases). Cool and dilute to 25 ml in a volumetric flask. Examine the solution and if turbid, filter through a double No. 40 paper. (Tin as metastannic acid, silicon as silica, and carbon if present will interfere). Measure the transmittance at 3900 Å against a reference solution about 1% below the expected nickel content.

Preparation of calibration graphs

Weigh high purity copper and nickel to give a total of 1.000 g with nickel in the appropriate range. To each beaker containing the appropriate proportions of copper and nickel, add 10 ml of nitric acid (s.g. 1.4) and continue as under *Procedure*.

A convenient chart (Fig. 1) covering nickel up to 40% has been constructed using a Beckman Model B spectrophotometer, a blue photo tube, no filter, a wavelength of 3900 Å, 2-cm tube-cells and a solution temperature of 20°. For this chart, standard solutions of copper and nickel were prepared with nickel contents ranging from 0 to 40% in 2% increments, the total weight of copper and nickel being 1 g. From these solutions calibration graphs were plotted using reference solutions containing 0, 2, 4, ... 30% nickel. The graphs give straight-line curves within the range shown on the chart. Beyond this range (*i.e.* mainly those solutions with less than 20% transmission) the curves tend to become asymptotic and hence fail to continue to follow Beer's Law.

It is also evident that the graphs are not parallel, because $\tan \theta = y/x$ is decreasing with increasing nickel concentration. This effect is probably characteristic of the spectrophotometer, in so far that the more dense the colour, the greater the slit opening required to zero the instrument resulting in an increased band width.

By introducing "sensitivity" lines it is possible to dispense with a reference solution to zero the instrument for nickel determinations of unknown content up to 33%. These "sensitivity" lines were constructed by taking solutions up to 6% nickel and setting these known solutions at 100% transmittance at the maximum sensitivity, position 4. After removing the cell containing the solution, the sensitivity is retarded to position 3 and the transmittance read. A plot of these readings gives the line sens. 3, Fig. 1. Similarly, by taking solutions of known nickel content 3 to 13% and reading the transmittance at sensitivity 2, the line sens. 2 is plotted. The line sens 1 is similarly plotted, by taking nickel solutions 10 to 20% and setting these solutions at 100% transmittance and sensitivity 4. After removing the cell containing the solution take the transmittance readings at a sensitivity of 1.

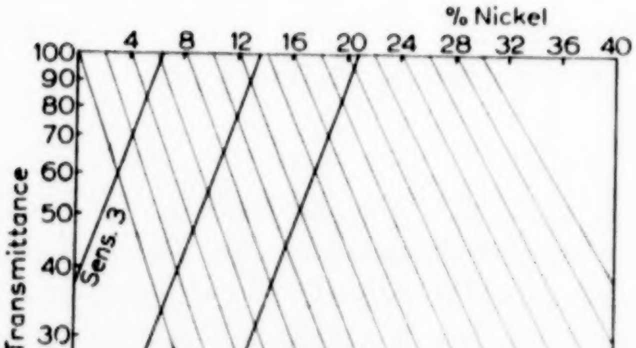

Fig. 1. Calibration graph (semi log.) for nickel nitrate in solutions of copper–nickel alloys.

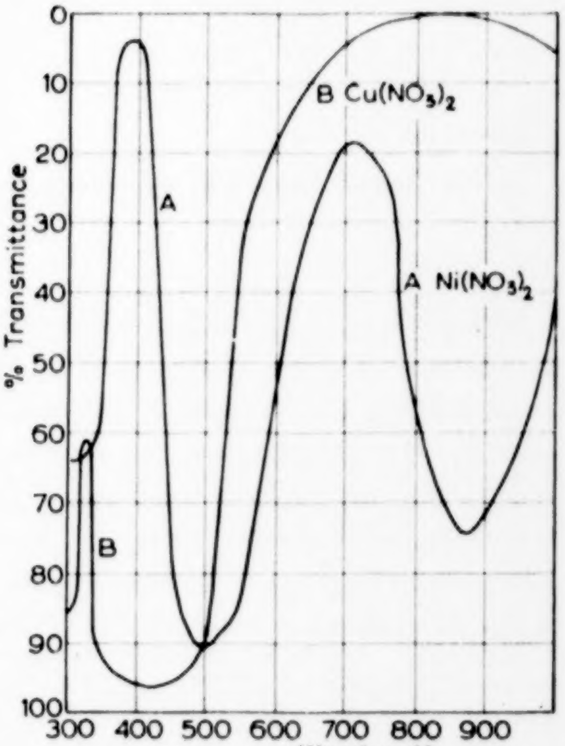

Fig. 2. Absorption spectra of nickel nitrate 2.65% solution, Curve A and of copper nitrate 2.5% solution, Curve B.

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Now if the nickel content of an unknown copper–nickel alloy is to be determined, prepare the solution according to the *Procedure*. Then switch the spectrophotometer to sensitivity position 2. (This gives a range from 0 to 23.5% nickel).

An arbitrary standard, say between 0 and 13% nickel, is chosen. Take for example 10%. Then 10% nickel at sensitivity 2 on the chart is 58% transmittance. With no solution in the instrument adjust the transmittance scale to read 58. Insert the cell containing the solution and measure the transmittance at sensitivity 4. If this transmittance measurement is greater than 100%, then the nickel content of the unknown is less than 10% and a lower arbitrary standard is selected. If the transmittance is less than 20%, the nickel content is greater than 21% and a higher arbitrary standard is taken. Any transmittance measurement between 20 and 100% will give the nickel content of the unknown for this example.

If the percentage nickel of the unknown is between 10 and 15%, a satisfactory accurate measurement is obtained, otherwise it is advisable to take an arbitrary standard just below (not more than 2%) the estimated nickel content.

The finding of an appropriate arbitrary standard can be found in a matter of seconds.

This manner for determining nickel is in principle the reverse of that for the construction of the chart using "sensitivity" lines. It is, however, not applicable for accurate determinations of nickel greater than 25% using the Beckman Model B unless a photomultiplier is used.

Normally for routine analysis, the usual calibration graph is used with an appropriate reference solution of known nickel content.

Comparison of methods

A comparison of results from gravimetric dimethylglyoxime methods, polarographic methods and the described procedure is given in Table I.

RESULTS

Transmission curves

Transmission curves were plotted from a 2.65% nickel nitrate solution in water and a 2.5% copper nitrate solution in water (Fig. 2). Curve A shows that nickel nitrate has two absorbance peaks in the visible range, a maximum at 3900 Å and one at 7100 Å. Copper nitrate, curve B, has absorbance peaks at 3320 Å and a maximum at 8300 Å. Nitric acid does not disturb the curves. Copper chloride absorbs strongly at 3900 Å and the intensity is dependent on the chloride ion concentration[1], therefore chloride ions must be absent. Hence a wavelength of 3900 Å is suitable for measuring the absorbance of nickel nitrate solutions. The molecular extinction coefficient for nickel nitrate at this wavelength is 5.6.

Interfering elements

Of the elements which might be expected in copper–nickel alloys, tin, silicon and carbon are the only ones which will interfere with the method and these when present are filtered off. Interference from iron as ferric phosphate is negligible. When urea was used to remove nitrous oxides it was found that varying amounts of permanganate were formed. Ultimately, experimental work showed that by adopting the technique

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described in the procedure, *i.e.* by cooling somewhat before adding phosphoric acid, any formation of permanganate was avoided. This indicates the probability that no perphosphoric acids were formed to cause oxidation.

Temperature

Nickel nitrate is somewhat temperature dependent. An error of ±0.025% nickel will occur for every 1° change in temperature, therefore the temperature of the sample should be within 1° of the temperature of the calibration. This is comparable to the temperature dependence of nickel perchlorate[2].

TABLE I

COMPARISON OF RESULTS BY DIFFERENT METHODS

% Mn	*% Fe*	*% Ni found by:*		
		Gravimetric (Dimethylglyoxime)	*Polarographic method*	*Proposed method*
—	—	1.01	1.06	1.00
—	—	1.82	1.72	1.79
0.63	1.17	5.06	5.16	5.10
0.70	1.20	5.82	6.00	5.90
0.99	1.42	10.10	10.30	10.03
0.86	1.30	11.16	11.40	11.10
1.14	0.62	29.94	30.10	30.00
1.50	0.94	31.82	31.70	31.85

SUMMARY

Nickel in copper–nickel alloys is determined as nitrate by precision photometry using a wavelength of 390 mμ. Nitrites, permanganate and insoluble particles such as metastannic acid and silica will interfere but these are readily removed. Chlorides, however, must be absent. A single determination can be completed within 5 min.

RÉSUMÉ

Une méthode photométrique rapide est proposée pour le dosage du nickel, sous forme de nitrate. Ce procédé peut s'appliquer en particulier aux alliages cuivre–nickel.

ZUSAMMENFASSUNG

Es wird eine photometrische Schnell-methode zur Bestimmung von Nickel in Form von Nickelnitrat beschrieben. Das Verfahren eignet sich besonders für Kupfer–Nickel Legierungen.

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POLAROGRAPHY OF LEAD IN HYDROXIDE AND CYANIDE MEDIA

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INTRODUCTION

Lead has long been known to give a polarographic wave in the presence of excess cyanide[1] and cyanide media have been recommended by a number of authors as suitable supporting electrolytes for the determination of lead in alloys[2-4]. It has usually been assumed that the lead is present in the form of a cyanide complex and a tentative estimate of the formation constant has been given[5]. Some preliminary experiments performed at the University of Kansas[6] suggested that the characteristic behavior of lead in cyanide media was due to the presence of biplumbite ion rather than cyanide complexes, and the present investigation was undertaken to clarify this question.

The polarography of lead in sodium hydroxide medium was first studied in a classic investigation by LINGANE in 1941[7]. He showed the reduction to be reversible and the biplumbite ion to be the prevalent species in the range of about 0.01 to 1.0M hydroxide ion. For the purposes of the present investigation it was felt desirable to redetermine more exactly the halfwave potential of lead as a function of hydroxide ion concentration, particularly in the range of 0.01 to 0.05M, under conditions of constant ionic strength and negligible liquid junction potentials.

APPARATUS AND REAGENTS

Polarograms were determined using a Sargent Model XXI without damping. The potential at the beginning and at the end of each polarogram was measured to ± 0.1 mV with a Rubicon precision potentiometer, thus calibrating the scan voltage more accurately than would be possible using only the meters on the polarograph. Current measurements were made at the point of maximum drop size. The addition of a maximum suppressor was found to be unnecessary. Half-wave potentials were determined graphically and, where highest accuracy was desired, from plots of log $[(i_d - i)/i]$ *vs.* E. The capillary was made from commercial marine barometer tubing ($m^{2/3}t^{1/6} = 1.59$ at -0.7 V *vs.* SCE in 1 N sodium hydroxide). Cell resistances were measured using an A. C. conductivity bridge. The reference cell potentials were determined with a Rubicon potentiometer.

All solutions were prepared with boiled, distilled water from reagent-grade chemicals. Sodium carbonate was excluded from the sodium hydroxide by dilution of supernatant liquid from a 10 N sodium hydroxide solution in which the sodium carbonate had been allowed to settle. Sufficient lead nitrate was added to make each solution $5.00 \cdot 10^{-4}M$ in lead. This amount of lead was found to give a precipitate in 2M sodium cyanide solution, and the supernatant liquid was used without disturbing the flocculent white precipitate. Samples were deaerated using prepurified tank nitrogen and held at 25.0° in a water thermostat.

RESULTS AND DISCUSSION

The mercury–mercuric oxide reference electrode

The use of a convenient reference electrode without a liquid junction potential was felt to be desirable and therefore the mercury/mercuric oxide electrode was selected. In order to check the potential of this electrode as a function of hydroxide ion concentration at constant ionic strength, measurements were made of the potential of the cell

$$\mathrm{Hg}\left|\,\mathrm{HgO}\,\right|\begin{matrix}\mathrm{NaClO_4}(2-x)M\\ \mathrm{NaOH}\ x\ M\end{matrix}\Big\|\ \mathrm{S.C.E.}$$

The mercury/mercuric oxide half-cell was prepared by stirring mercury, yellow mercuric oxide, and the appropriate hydroxide–perchlorate mixture together and allowing to stand for at least 20 min for equilibration. The potential was usually found to be stable after this time but drifting occasionally occurred. It was observed that the potential would reach the equilibrium value and become stable more satisfactorily if a current of a few μA were passed anodically through the half-cell for a few moments. The results of the measurements of the stable half-cell potential against the saturated calomel electrode are given in Table I and a plot of E *versus* log(OH$^-$) is shown in Fig. 1. The variation of potential with pOH is seen to be linear over a range of 0.25 to 2.0 pOH units and the slope, 0.0614 V/pOH, is close to the theoretical value of 0.0591. Variation in the junction potential between the mercury oxide half-cell and the calomel electrode is evidently not serious over this range. The potential of the electrode at 0.0100N sodium hydroxide and 1.99M sodium perchlorate was

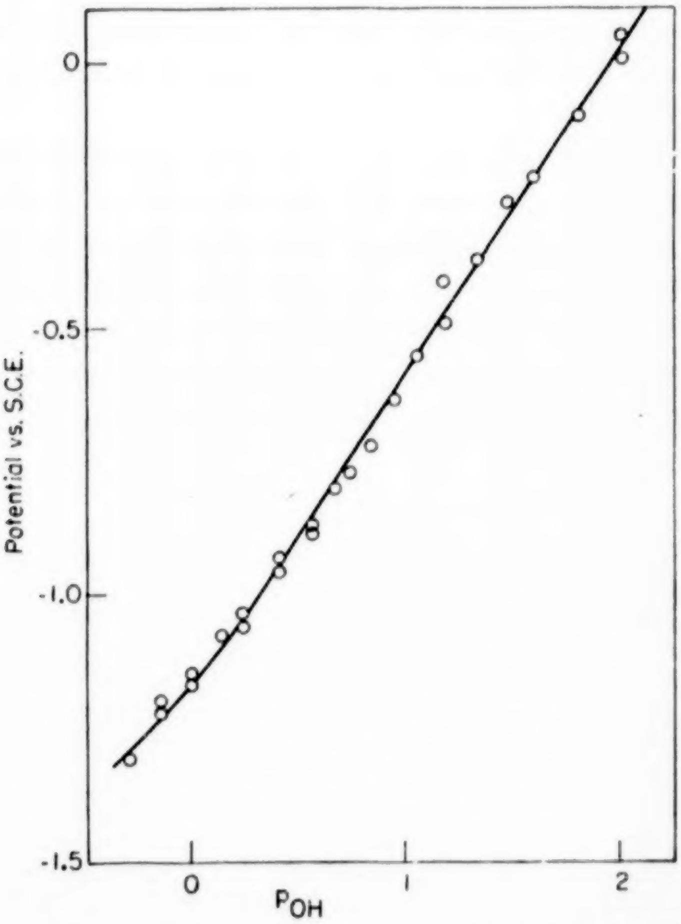

Fig. 1. Potential of the mercury–mercuric oxide electrode *versus* the S.C.E., as a function of pOH. Ionic strength made up to 2.00M with sodium perchlorate.

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TABLE I

POTENTIAL OF THE MERCURY–MERCURIC OXIDE REFERENCE HALF-CELL

C_{OH^-}[a]	*E (V vs. S.C.E.)*	
	1st run	*2nd run*
2.00	—0.131	
1.43	—0.122	—0.120
1.00	—0.115	—0.117
0.718	—0.108	
0.572	—0.106	—0.104
0.387	—0.093	—0.096
0.276	—0.087	—0.088
0.214	—0.080	
0.182		—0.078
0.148	—0.072	
0.113		—0.062
0.087	—0.055	
0.066	—0.049	—0.041
0.047	—0.037	
0.033		—0.026
0.025	—0.022	
0.016		—0.011
0.010	+0.001	+0.005

[a] Ionic strength made up to 2.00*M* with sodium perchlorate as required.

found to be +0.002 V *versus* the S.C.E. The standard potential given in the literature[8] is not directly utilizable for polarography because values for the activity coefficients involved are not known. From the standpoint of convenience, stability and reproducibility, the electrode may be recommended for polarographic work.

Polarography in hydroxide media

Polarograms were determined using cells of the type

$$\mathrm{Hg,\ HgO_{(s)}}\left|\begin{array}{lr}\mathrm{NaClO_4} & 2.0\text{-}xM\\ \mathrm{NaOH} & xM\\ \mathrm{Pb(NO_3)_2} & 5\cdot10^{-4}M\end{array}\right|\mathrm{D.M.E.}$$

where x varied from 0.01 to 2.00*M*.

Small amounts of lead nitrate were found to have no effect upon the potential and therefore the same electrolyte was used throughout the cell, which was an H-type polarograph cell with a coarse fritted glass partition. The resistance of the solution in this apparatus varied between 100 and 140 ohms, depending on the hydroxide concentration. With such low resistances, the iR drop correction was less than 0.4 mV and was neglected.

The findings in sodium hydroxide media are summarized in Table II. Study of the polarography of lead confirms the general conclusions reached by LINGANE[7]

TABLE II

HALF-WAVE POTENTIAL OF BIPLUMBITE ION IN SODIUM HYDROXIDE

C_{OH^-}[a]	$E_{1/2}$	i_d[b]
2.00	0.762	2.62
1.43	0.752	2.69
1.00	0.744	2.72
0.744	0.734	2.78
0.564	0.726	2.82
0.431	0.715	2.83
0.327	0.705	2.86
0.208	0.689	2.79
0.142	0.675	2.82
0.0710	0.646	2.76
0.0482	0.629	2.74
0.0330	0.615	2.63
0.0174	0.592	2.47
0.0100	0.577	2.43
0.0096	0.576	2.36
0.002	0.552	1.96[c]

[a] Ionic strength made up to 2.00*M* with sodium perchlorate as required.
[b] Biplumbite concn. is $5 \cdot 10^{-4} M$.
[c] Irreversible reduction wave.

regarding the reversibility of the electrode reaction at hydroxide concentrations greater than 0.01*M* and the identity of the biplumbite ion as the species present. The results show, however, that by elimination of liquid junction potentials and use of a constant ionic-strength medium a slope for the plot of half-wave potential *vs.* pOH is obtained which is very close (87.5 mV/pOH) to the theoretical value of 89 mV/pOH. The half-wave potential of biplumbite ion in 1.00*N* sodium hydroxide at an ionic strength of 2.00 is −0.744 V *vs.* the S. C. E. From our data the value 12.62 for the logarithm of the overall formation constant of the biplumbite ion at an ionic strength of 2.00 can be calculated. Previous literature values are 12.15 (polarography at variable ionic strength)[9], 13.34 (polarography in 1*M* nitrate medium)[10], 13.94 (solubility with extrapolation to zero ionic strength)[11] and 13.95 (polarography with extrapolation to zero ionic strength)[12].

Polarography in cyanide media

In order to determine whether a lead cyanide complex was detectable polarographically or not, polarograms were taken of lead solutions containing various concentrations of cyanide from millimolar to 2.00*M* and added hydroxide from 0.0 to 0.1*M*. It was observed that 0.5 m*M* lead was incompletely soluble in 1.0 and 2.0*M* sodium cyanide and that the lead waves in such solutions coalesced with the anodic dissolution of the mercury drop so that no characteristic half-wave potential of the lead species could be determined. The characteristic wave of biplumbite ion in solutions containing sodium hydroxide did not appear to be affected by the addition of small amounts of cyanide. At hydroxide concentrations lower than 0.01*M*, with no cyanide present, the reduction waves were no longer reversible.

In order to look for evidence of a cyanide complex under the most favorable conditions possible, polarograms were run on solutions which were $0.01 M$ in hydroxide and contained varying amounts of cyanide, using a cell which eliminated uncertainties due to liquid junction potentials. The hydroxide concentration was felt to be the lowest which would give a reversible reduction but yet might allow formation of a lead cyanide complex by competition of cyanide with hydroxide for the lead.

The following cell was used:

Hg, $HgO_{(s)}$	$0.01 N$ NaOH $1.99 M$ $NaClO_4$ $5.00 \cdot 10^{-4} M$ $Pb(NO_3)_2$	$x M$ NaCN $0.01 M$ NaOH $1.99 - x M$ $NaClO_4$ $\sim 4 \cdot 10^{-4} M$ $Pb(NO_3)_2$	D.M.E.

An H-type polarographic cell fitted with an exceedingly fine fritted glass partition served to keep the two solutions from mixing and thereby exclude cyanide from the reference half-cell. The resistance of this cell being approximately 200 ohms, the accompanying iR drop of 0.0005 V could be neglected in interpreting results. As will be seen from the results shown in Fig. 2 and tabulated in Table III, no indication of a cyanide complex was detectable. At sufficiently low concentrations, the anodic wave of cyanide gave a well-defined diffusion current, and showed the characteristics reported for it in the literature[13]. At cyanide concentrations greater than $0.03 M$, the anodic dissolution potential of the mercury drop became more negative than the potential of the biplumbite ion and the lead wave is obscured by the anodic cyanide wave.

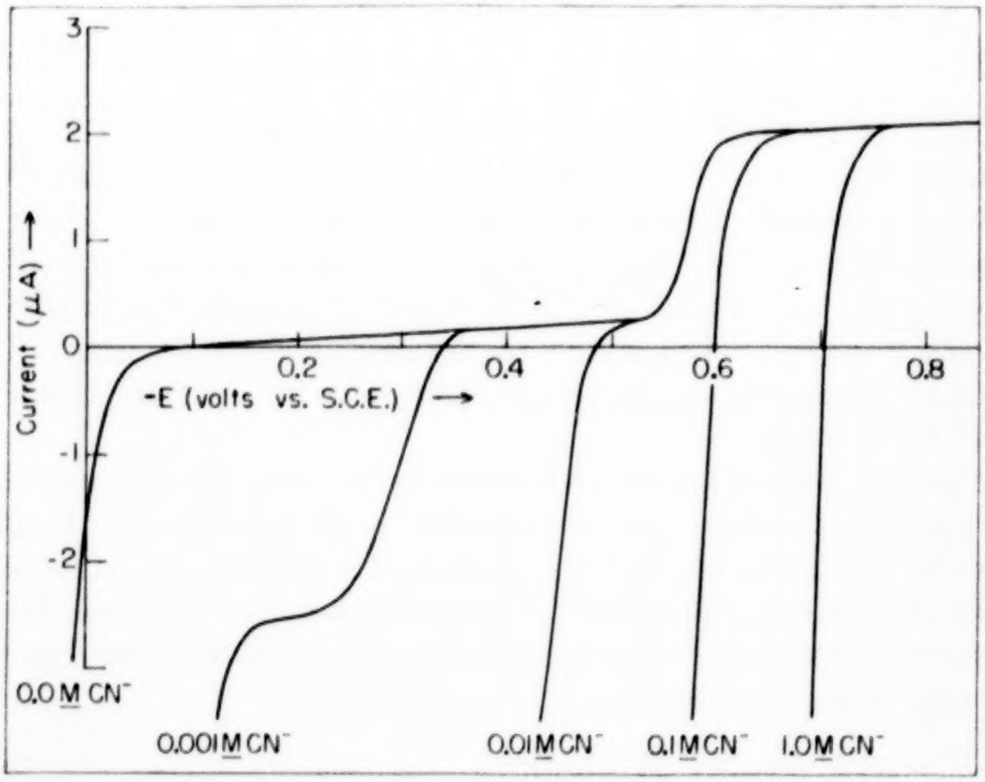

Fig. 2. Polarograms of lead in $0.01 N$ sodium hydroxide with various amounts of added cyanide. Ionic strength made up to $2.00 M$ with sodium perchlorate.

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TABLE III

HALF-WAVE POTENTIAL OF LEAD *vs.* S.C.E. AS A FUNCTION OF CYANIDE AND HYDROXIDE ION CONCENTRATION

C_{OH^-} [a]	C_{CN^-}	$E_{1/2}$
0.01	—	—0.573
0.01	0.010	—0.573
0.01	0.015	—0.574
0.01	0.020	—0.572
0.01	0.025	—0.573
0.01	0.030	—0.572
0.01	0.100	—0.61 [b]
0.01	1.00	—0.72 [b]
0.01	2.00	—0.74 [b]
0.1	1.00	—0.72 [b]
—	1.00	—0.72 [b]
—	2.00	—0.74 [b]
—	1.00	—0.72 [c]

[a] Actual OH^- added.

[b] Potential determined at $^1/_2$ cathodic current.

[c] $\mu = 1$; all other solutions, $\mu = 2$.

Because 0.5 m*M* lead was incompletely soluble in 2*M* cyanide, the solubility of lead in this medium could be determined using the diffusion current data from Table II. Two separate determinations yielded values of $2.48 \cdot 10^{-4}$ and $2.55 \cdot 10^{-4} M$ lead for the solubility in 2*M* sodium cyanide. Although a basic lead cyanide is known to be formed under these conditions[6], these values agree quite closely with the value $3.2 \cdot 10^{-4} M$ which can be calculated from the equilibrium data of GARRETT, VELLENGA AND FONTANA[11] assuming the lead to be dissolved by hydroxide ions from the hydrolysis of the cyanide.

In published procedures for the determination of lead using cyanide media, invariably a mixture containing excess hydroxide ion has been used[2-4]. It is evident from the present work that the lead wave obtained is actually that of biplumbite ion, a fact which only MILNER[4] appears to have suspected. The presence of cyanide in these procedures is desirable, however, because it acts as a masking reagent to prevent the interference of other metals.

ACKNOWLEDGEMENT

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SUMMARY

The polarographic reduction wave of lead in cyanide-supporting electrolytes has been shown to be due to the presence of the biplumbite ion. No evidence for a lead–cyanide complex in aqueous solution has been found. The polarographic characteristics of lead in alkaline solutions have been redetermined in media of constant ionic strength using cells without liquid junction potentials. The mercury/mercuric oxide electrode has been studied and its use as a reference electrode in polarography is recommended.

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RÉSUMÉ

Les auteurs ont étudié la réduction polarographique du plomb, en présence de cyanure, comme électrolyte de base. Ils recommandent l'emploi de l'électrode mercure/oxyde mercurique, comme électrode de référence.

ZUSAMMENFASSUNG

Es wird die polarographische Reduktion von Blei in Gegenwart von Cyanid als Elektrolyt untersucht. Als Referenzelektrode wird eine Quecksilber/Quecksilberoxyd Elektrode empfohlen.

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DOSAGES EN ANALYSE MINÉRALE PAR EXTRACTION À L'AIDE DE CATIONS COLORÉS

I. INTRODUCTION

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On a proposé depuis longtemps l'utilisation de cations organiques pour effectuer l'extraction à l'aide de solvants convenablement choisis, d'anions divers: organiques (RCO_2^-, $ArSO_3^-$, ArO^- etc.) et minéraux simples (I^-) ou complexes (ClO_4^-, $SbCl_6^-$, $AuCl_4^-$, etc.).

Les cations organiques utilisés sont les suivants: Ammonium (RNH_3^+, $R_2NH_2^+$ . . . R_4N^+), Oxonium (ROH_2^+, R_2OH^+, R_2COH^+), Diazonium (RN_2^+), Arsonium (R_4As^+), Stibonium (R_4Sb^+), Phosphonium (R_4P^+), Sélénonium (R_3Se^+), Sulfonium (R_3S^+).

Le nombre des associations possibles anion + cation est donc très grand, ce qui explique le large développement que connaît actuellement cette méthode[1].

Mais ces cations sont en général incolores. Ils sont associés le plus souvent à des anions incolores ou peu colorés; la phase organique obtenue après extraction est donc elle-même incolore ou peu colorée. Il est donc impossible d'effectuer directement une spectrocolorimétrie du corps extrait (en lumière visible). Si l'on désire réaliser simultanément la séparation et le dosage par spectrocolorimétrie dans le visible, il faut

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utiliser des cations organiques ou organo-métalliques colorés. De plus, la mise au point de dosages de traces, ou l'emploi des techniques microchimiques, entraine l'utilisation de cations de coloration intense.

Deux groupes de cations sont alors utilisables:

(1) Les complexes que donnent certains cations métalliques (Fe^{+2}, Co^{+2}, Cu^{+2}...) avec des bases organiques comme l'*o*-phénanthroline[2] et ses dérivés: bathophénanthroline[3], néocuproïne[4-7], bathocuproïne[6,8,9] la 2-2'-diquinoline[10-13], ou l'*a*-*a*'-dipyridyle et ses dérivés[14]. On peut les utiliser pour séparer et doser, soit les éléments métalliques complexés, soit les anions associés.

(2) Les cations correspondants aux colorants basiques.

Tout colorant renfermant une fonction basique (c'est le plus souvent une fonction amine) peut donner à partir d'un pH convenable un cation de couleur intense et généralement différente de celle de la molécule. Ces colorants sont parfois utilisés comme indicateur de pH (le rouge neutre par exemple).

Avec une fonction amine primaire, la réaction s'écrit:

$$ArNH_2 + H^+ \rightleftarrows ArNH_3^+$$

En désignant par B la molécule de colorant basique, on peut schématiser cette réaction par:

$$B + H^+ \rightleftarrows HB^+$$

C'est par cette formule que nous désignerons par la suite le cation coloré.

Quelques colorants[15-17], et en particulier le bleu de méthylène[18-25] sont utilisés pour le dosage par extraction des détergents et agents tenso-actifs. Dans les autres domaines de l'analyse, à l'exception de la rhodamine B [26] qui a été proposée pour le dosage de l'antimoine[27-35], de l'or[36], du gallium[37,38] et du thallium[39,40], les colorants basiques sont actuellement peu utilisés: une benzylidènerhodanine pour l'extraction de l'or[41,42], la *p*-nitrosodiméthylaniline pour la séparation et le dosage du platine et du palladium[43,44], le violet de méthyle pour le dosage des traces d'antimoine[45,46] et de thallium[47-50], le vert brillant également pour le thallium[48]. J'ai décrit précédemment[51] une méthode utilisant le bleu de méthylène: l'anion fluoborique BF_4^- associé à ce colorant est extractible par le dichloro-1,2-éthane, ce qui permet sa séparation de nombreux anions et le dosage de traces de bore.

D'autres exemples sont décrits dans les mémoires suivants.

RÉSUMÉ

Deux sortes de cations colorés sont utilisables pour le dosage par extraction d'anions divers simples ou complexes: (a) les cations du type *o*-phénanthroline ferreuse $Fe(o\text{-}ph)_3^{+2}$; ce sont surtout les dérivés de l'*o*-phénanthroline qui ont été utilisés; (b) les cations correspondants aux nombreux colorants basiques dont l'utilisation est jusqu'alors très limitée. Ils permettent des dosages d'une grande sensibilité.

SUMMARY

In the extraction method two kinds of coloured cations can be used for the determination of simple or complex anions: (a) *o*-Phenanthroline derivatives; (b) Cations of basic dyes. The method is especially suitable for the determination of trace elements.

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ZUSAMMENFASSUNG

Für die spektrocolorimetrische Bestimmung einfacher und komplexer Anionen nach dem Extraktionsverfahren sind 2 Gruppen von gefärbten Kationen verwendbar: (1) *o*-Phenanthrolin Derivate, (2) Kationen basischer Farbstoffe. Die diskutierte Methode ist besonders geeignet zur Bestimmung von Spurenelementen.

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DOSAGES EN ANALYSE MINÉRALE PAR EXTRACTION À L'AIDE DE CATIONS COLORÉS

II. UTILISATION DES COMPLEXES DE L'*o*-PHÉNANTHROLINE POUR LA SÉPARATION ET LE DOSAGE DE PETITES QUANTITÉS DE NICKEL EN PRÉSENCE DE FER ET DE COBALT

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RAPPEL DE FAITS CONNUS

On sait que l'*o*-phénanthroline donne avec certains cations des complexes très stables dans un large domaine de pH. Ceux des métaux ferreux en particulier ont fait l'objet d'études nombreuses et diverses: sur les vitesses de réaction, les constantes de stabilité, les mécanismes de dissociation et de racémisation, l'action des rayons X et γ, l'action biologique... etc. (fer[1-22], nickel[23-34], cobalt[35-38]). Par contre l'extraction de ces divers complexes n'a été que peu utilisée en analyse[39], alors que des dérivés de l'*o*-phénanthroline comme la bathophénanthroline[40], la néocuproïne[41-44] ou la bathocuproïne[43'45'46] ont fait l'objet dans ce domaines de plusieurs publications.

Nous rappelons que le fer(II) donne avec l'*o*-phénanthroline (*o*-ph) un complexe rouge très stable[1,3,4'5,10,11,16] de formule $Fe(o\text{-}ph)_3^{+2}$ que certains auteurs désignent sous le nom de „ferroïne". Le fer(III) donne également un complexe très stable, jaune-brun: $Fe(o\text{-}ph)_3^{+3}$.

Les oxydants de potentiel élevé comme le permanganate, le cérium(IV) oxydent la ferroïne en un complexe bleu[2,20,21]; le système est couramment employé comme indicateur d'oxydo réduction.

Le cobalt(II)[36,38] se comporte comme le fer(II); il donne un complexe jaune $Co(o\text{-}ph)_3^{+2}$ dont la forme oxydée est brune.

Le nickel présente des propriétés différentes. On a décrit trois complexes de formule générale $Ni(o\text{-}ph)_n^{+2}$ [31,32,34] ou n prend les valeurs 1[34] 2[32], 3[25,28,31] et dont les couleurs sont respectivement bleu, violet, lilas. Pour ces complexes, on ne connait pas de forme oxydée.

EXTRACTION DES COMPLEXES DE L'*o*-PHÉNANTHROLINE AVEC LES CATIONS DES MÉTAUX FERREUX*

Les complexes de formule $M(o\text{-}ph)_3^{+2}$ donnent avec certains anions comme I^-, SCN^-, $CCl_3CO_2^-$, des combinaisons extractibles quantitativement dans un large domaine de pH (0 à 7 environ) par les solvants suivants: alcool benzylique, dichloro-1, 2-éthane, *o*-nitrotoluène, *o*-bromotoluène. Le complexe du fer(III) se comporte de manière identique sauf avec l'iodure qui est oxydé en iode. D'autres anions comme

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* L. PATEAU – Thèse d'ingénieur D.P.E. CNAM Paris (non publiée).

BF_4^-, ClO_4^-, IO_4^- donnent des composés peu solubles dans l'eau, extractibles par l'un des solvants indiqués ci-dessus; par exemple les complexes $M(o\text{-ph})_3^{+2}$ et $Fe(o\text{-ph})_3^{+3}$ associés à l'anion perchlorique ClO_4^-, sont extractibles par l'alcool benzylique, l'*o*-nitrotoluène et l'*o*-bromotoluène; associés à l'anion fluoborique BF_4^-, par l'alcool benzylique.

Par contre, les formes oxydées de la ferroïne et du complexe du cobalt (II) ne sont pas extractibles.

Nous avons utilisé ces diverses propriétés pour la séparation et le dosage du nickel.

DOSAGE DU NICKEL EN PRÉSENCE DE FER ET DE COBALT

Principe

Nous supposerons que la solution acide renferme les cations Fe^{+3}, Co^{+2}, Ni^{+2}. Après réduction de Fe^{+3} par le métabisulfite, on ajoute un excès d'*o*-phénanthroline: les complexes de formule générale $M(o\text{-ph})_3^{+2}$ se forment. L'addition de cérium(IV) en excès fait passer les complexes du fer(II) et du cobalt(II) sous forme oxydée. Dans ces conditions, seul le nickel (II) reste extractible si l'on associe le complexe à l'un des anions cités précédemment. La présence d'un excès de sels cériques empêche l'utilisation des anions et solvants réducteurs: I^- SCN^-, alcool benzylique, dérivés du toluène. Nous avons donc choisi l'anion trichloracétique et comme solvant, le dichloro-1,2-éthane. La réaction est quantitative:

$$\mathrm{Ni}(o\text{-ph})_3^{+2} + 2\ \mathrm{CCl_3CO_2^-} \underset{2}{\overset{1}{\rightleftharpoons}} (\mathrm{CCl_3CO_2})_2\ \mathrm{Ni}(o\text{-ph})_3$$

sym.-dichloro-1,2-éthane

L'expérience montre d'autre part que les résultats obtenus sont plus précis, si, après extraction du nickel, la phase organique est séparée et agitée pendant quelques minutes avec une solution diluée de cérium(IV) qui oxyde les dernières traces de fer qu'elle renferme. On ajoute à cette solution de l'acide trichloracétique et de l'*o*-

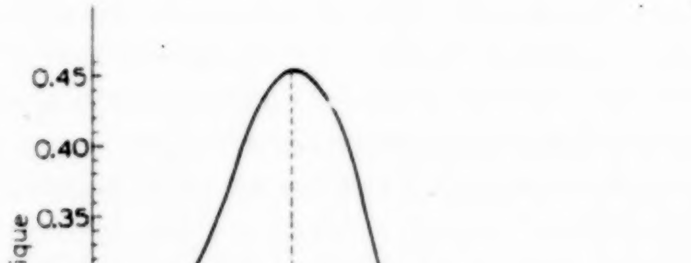

Fig. 1. Spectre d'absorption du trichloracétate d'*o*-phénanthroline de nickel(II) dans le dichloro-1,2-éthane.

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phénanthroline pour éviter le déplacement de l'équilibre précédent dans le sens 2. L'expérience montre qu'au cours de cette opération, le nickel ne passe pas dans la couche aqueuse.

Le spectre d'absorption de la combinaison extraite par le dichloro-1,2-éthane (à 20°), est représenté sur la Fig. 1; le maximum est situé à 520 mμ. L'appareil utilisé est le spectrophotomètre Jobin et Yvon, type ,,Algérie".

Mode opératoire

Nous avons adopté le mode opératoire ci-dessous, applicable par exemple à 5 ml de solution sulfurique ou chlorhydrique amenée à un pH voisin de 1, et renfermant au plus 15 à 16 mg de métal ou d'alliage, dont 5 mg de fer au maximum. La présence d'ions nitrates est incompatible avec le principe du dosage qui suppose la réduction de Fe^{+3} en Fe^{+2}. Pour éviter la présence de ces ions, l'attaque du métal ou de l'alliage peut être effectuée à l'ébullition par l'acide sulfurique 9*N* auquel on ajoute peu à peu de l'eau oxygénée à 110 volumes. L'excès de ce réactif est ensuite détruit par ébullition prolongée. Après refroidissement, la solution est amenée à un pH voisin de 1.

Réactifs utilisés

Solution étalon de nickel. Le sel de nickel utilisé est le sulfate ,,Prolabo R.P." $NiSO_4$, 7 H_2O amené à poids constant par chauffage au four électrique à 450°. Par pesée, on prépare une solution dans H_2SO_4 *N*/10 renfermant exactement 2 g de nickel par l, soit 2 mg/ml.

Solution de métabisulfite. Solution aqueuse à 5% du sel de potassium pur, préparée au moment de l'utilisation.

Solution d'o-phénanthroline. Solution aqueuse environ *M*/10, obtenue en dissolvant 5 g de base pure dans 25 ml d'acide sulfurique normal que l'on dilue ensuite à 250 ml avec de l'eau distillée. Elle est conservée à l'abri de la lumière.

Solution de cérium. a) Solution aqueuse de sulfate cérique environ *M*/10 dans l'acide sulfurique *N*.

b) Solution aqueuse de sulfate cérique environ *M*/100 dans l'acide sulfurique 2*N*/10.

Solution d'acide trichloracétique. Solution aqueuse *M*/2 du produit pur (8% environ).

Dichloro-1,2-éthane. Le produit commercial pur est redistillé; on recueille la fraction distillant à 83 ± 1°.

A 5 ml de la solution à analyser, ajouter 0.5 ml de solution de métabisulfite, et attendre environ 1 min. Ajouter ensuite 10 ml de solution d'*o*-phénanthroline et attendre 5 min. La solution cérique *M*/10 est ensuite ajoutée goutte à goutte, en agitant, jusqu'au virage de la ferroïne (apparition de la forme oxydée bleue). Si la solution ne renferme pas de fer, on peut ajouter 1 ml de la solution d'*o*-phénanthroline ferreuse utilisée habituellement comme indicateur d'oxydo-réduction. Ajouter encore 2 ml de la solution cérique, puis 3 ml de la solution d'acide trichloracétique. Placer ce mélange dans une ampoule à décanter de 125 ml avec 10 ml de dichloro-1,2-éthane, et agiter énergiquement pendant 3 min environ. Après décantation, la phase organique est séparée et placée dans une autre ampoule à décanter avec le mélange suivant qui constitue la solution de lavage: 10 ml de la solution cérique *M*/100, 1 ml de la solution d'*o*-phénanthroline et 1 ml de la solution d'acide trichloracétique. Agiter énergiquement pendant 2 min; après décantation, séparer la phase organique, la centrifuger, et effectuer la mesure de la densité optique pour $\lambda = 520$ mμ.

Essai à blanc

Il est effectué en remplaçant la solution à doser par 5 ml d'acide sulfurique *N*/10. Sa densité optique est en général très faible (0.015 à 0.020); elle n'est pas dûe aux

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traces de nickel que renferment les réactifs, mais à une faible quantité de produits colorés jaunes qui sont vraisemblablement des impuretés de l'*o*-phénanthroline.

Étalonnage

On applique le mode opératoire précédent en remplaçant la solution à doser par des mélanges connus de la solution étalon de nickel et d'acide sulfurique *N*/10. La loi de Beer est suivie comme le montre la droite d'étalonnage de la Fig. 2, obtenue à 22°, en utilisant une cuve de 2 cm d'épaisseur.

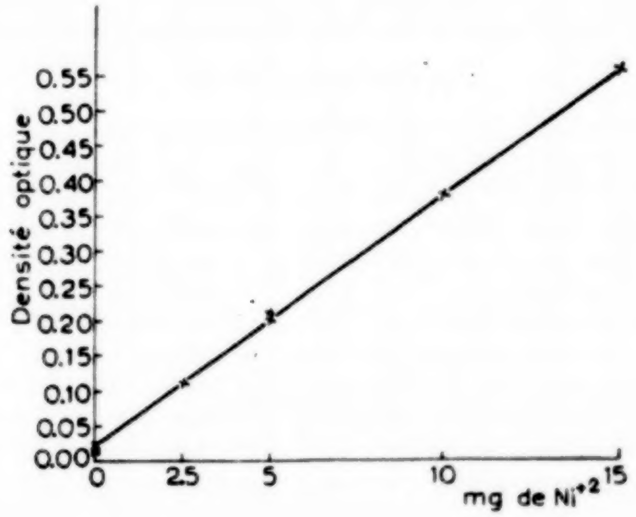

Fig. 2. Courbe d'étalonnage pour le dosage du nickel.

Précision

Pour une densité optique voisine de 0.50, les résultats sont reproductibles à 0.005 unité près, ce qui permet de doser 10 mg de nickel avec une erreur relative voisine de 1%. Les résultats du dosage du nickel en présence de quantités variables de fer et de cobalt sont rassemblés dans le Tableau 1. Nous avons utilisé des volumes connus de solution d'alun de fer (Prolabo R.P.) et de sulfate de cobalt (Prolabo R.P.) renfermant 1 et 5 mg de métal par ml.

Cette méthode un peu moins précise que la gravimétrie classique, utilisant la diméthylglyoxime, présente sur celle-ci l'avantage d'une grande rapidité d'exécution.

TABLEAU I

Fe(mg)	*Co (mg)*	*Ni (mg) ajouté*	*Ni (mg) dosé*
0	0	15.00	15.10
1	1	5.00	5.10
		10.00	10.08
1	5	5.00	4.97
		10.00	10.07
5	1	5.00	5.04
		10.00	9.97
5	5	5.00	5.07
1	10	5.00	5.05

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RÉSUMÉ

Un exemple de séparation et de dosage par extraction à l'aide des complexes de l'*o*-phénanthroline est décrit: le complexe du nickel(II) associé à l'anion trichloracétique est quantitativement extractible par le dichloro-1,2-éthane, alors que les formes oxydées des complexes du fer(II) et du cobalt(II) ne le sont pas. La méthode, un peu moins précise que la gravimétrie classique utilisant la diméthylglyoxime, présente l'avantage d'une grande rapidité d'exécution.

SUMMARY

A rapid extraction method is described for the separation of nickel from iron and cobalt and the determination of Ni, in which *o*-phenanthroline is used as complexing agent.

ZUSAMMENFASSUNG

Es wird eine rasche Methode zur Trennung des Nickels von Eisen und Kobalt mit Hilfe von *ortho*-Phenanthrolin und die Bestimmung des Nickels nach dem Extraktionsverfahren beschrieben.

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THE RAPIDLY DROPPING MERCURY ELECTRODE IN DIRECT CURRENT AND ALTERNATING CURRENT POLAROGRAPHY

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INTRODUCTION

In direct current (D.C.) polarography, the dropping mercury electrode (DME), which has a drop time between about 3 and 6 sec under the applied pressure of 30 to 60 cm of mercury, is usually employed as an indicator electrode. When the drop time is less than 1.5 sec, polarographic currents are generally disturbed by the vortex motion of the mercury of the electrode, *i.e.*, "Spüleffekt"[1].

The same electrode as in D.C. polarography has also been used in alternating current (A.C.) polarography. However, when the A.C. polarogram is recorded automatically with such an electrode, the true peak current is often skipped because of the relatively long drop time in comparison with the scanning rate of the applied voltage. In order to record the true peak current, therefore, the scanning rate must be made very slow, or better, the current must be measured point by point by manual operation. It has been found that this deficiency can be overcome by using the rapidly dropping mercury electrode (RADME) whose drop time is shorter than 1 sec.[2]

For this reason, it seemed desirable and worthwhile to reinvestigate the characteristics of the RADME, which hitherto has been considered to be an unsuitable electrode for polarographic studies. In this paper, some results of the application of the RADME to D.C. and A.C. polarography are presented, and the potentialities of the RADME in polarographic analysis are discussed.

REAGENTS AND APPARATUS

The lead solution was prepared by dissolving lead nitrate; it was standardized gravimetrically as lead sulphate. The standard solution of cadmium was prepared by dissolving a known amount of pure cadmium metal in nitric acid. All other chemicals used were analytical reagent grade. Redistilled water was used for the preparation of the solutions.

All D.C. polarograms were obtained with a manual polarograph[3] and the A.C. polarograms were recorded with a Yanagimoto Y-GR Model 2 Galvarecorder. The drop time and the rate of flow of mercury of the DME used were 5.41 sec and 1.824 mg/sec, respectively, which were measured in air-free 0.1 *M* potassium nitrate solution under an applied pressure of 55 cm of mercury at —0.50 V *vs.* S.C.E. Two RADME's were used, which had drop times of 0.86 and 0.98 sec and rates of flow of mercury of 16.98 and 16.83 mg/sec, respectively, measured under an applied pressure of 40 cm of mercury in the same solution and at the same potential as in the case of the DME. A saturated calomel electrode with a large area was used as the anode, which was connected to the cell solution by a HUME AND HARRIS-type agar bridge[4]. All measurements were carried out in a thermostat of 25.00° ± 0.01°. The dissolved oxygen in the solution was expelled by passing pure nitrogen gas through the solution before measurement. In the A.C. polarographic measurements, a platinum electrode with a large area was inserted into the solution as the third electrode and this was connected to the anode through a condenser of 100 μF in order to keep the impedance of the electrolysis cell as low as possible[5].

RESULTS AND DISCUSSION

D.C. polarography

In the absence, or at very low concentration, of a surface-active substance, such as polyoxyethylene lauryl ether (LEO) or gelatin, maxima of the second kind were generally observed on the current–voltage curves obtained at the RADME. For example, the limiting current of mercuric ion at the RADME showed a maximum value near the potential of the electrocapillary zero and decreased markedly both at the more positive and negative potentials (Fig. 1). This maximum was completely suppressed by the addition of $2 \cdot 10^{-4} M$ LEO, and the further addition of LEO had little effect on the value of the limiting current. Such phenomena were also observed in the reduction of lead and cadmium ions at the RADME in $0.1 M$ potassium nitrate solution (Figs. 2 and 3).

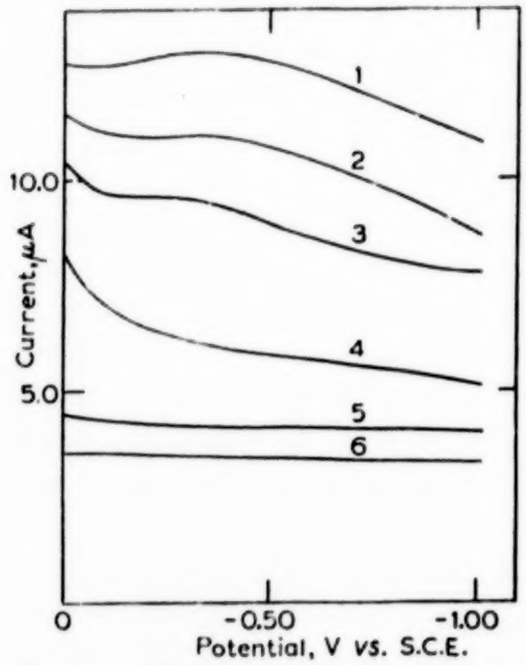

Fig. 1. Current–voltage curves of $2 \cdot 10^{-4} M$ Hg(II) in $0.1 M$ HNO_3 solutions in the absence and in the presence of LEO. Concentration of LEO: (1) 0; (2) $1 \cdot 10^{-6} M$; (3) $2 \cdot 10^{-6} M$; (4) $2 \cdot 10^{-5} M$; (5) $1 \cdot 10^{-4} M$; (6) $4 \cdot 10^{-4} M$.

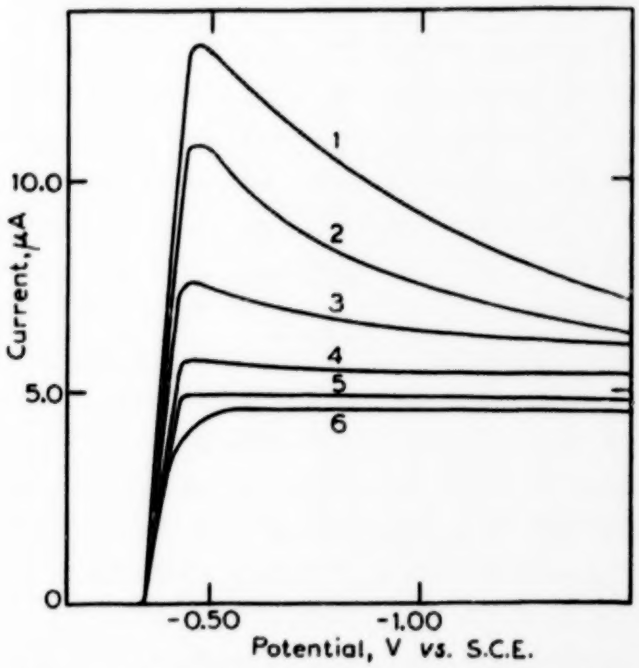

Fig. 2. Current–voltage curves of $2 \cdot 10^{-4} M$ Pb(II) in $0.1 M$ KNO_3 solutions in the absence and in the presence of LEO. Concentration of LEO: (1) 0; (2) $2 \cdot 10^{-6} M$; (3) $1 \cdot 10^{-5} M$; (4) $2 \cdot 10^{-5} M$; (5) $5 \cdot 10^{-5} M$; (6) $5 \cdot 10^{-4} M$.

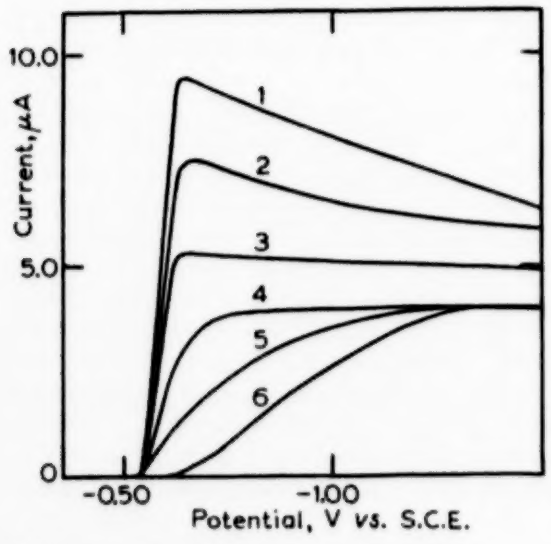

Fig. 3. Current–voltage curves of $2 \cdot 10^{-4} M$ Cd(II) in $0.1 M$ KNO_3 solutions in the absence and in the presence of LEO. Concentration of LEO: (1) 0; (2) $5 \cdot 10^{-6} M$; (3) $2 \cdot 10^{-5} M$; (4) $7 \cdot 10^{-5} M$; (5) $2 \cdot 10^{-4} M$; (6) $4 \cdot 10^{-4} M$.

TABLE I

DIFFUSION COEFFICIENTS CALCULATED BY APPLYING THE MODIFIED ILKOVIC EQUATION TO THE LIMITING CURRENTS AT THE RADME

Maximum suppressor	*Height of mercury column* cm	*Pb(II)*[a]		*Cd(II)*[a]		*$Fe(C_2O_4)_3^{3-}$*[b]	
		Drop time sec	$D \times 10^6$ cm^2/sec	*Drop time* sec	$D \times 10^6$ cm^2/sec	*Drop time* sec	$D \times 10^6$ cm^2/sec
0.1% gelatin	30	1.01	6.15	1.01	6.38	1.15	4.37
0.1% gelatin	50	0.61	6.07	0.61	6.25	0.68	4.25
$5 \cdot 10^{-4}M$ LEO	50	0.57	8.00	0.57	6.76		

[a] In $0.1M$ KNO_3.
[b] In $0.5M$ $K_2C_2O_4$.

The apparent values of the diffusion coefficients of lead, cadmium and trioxalatoferrate(III) ions in the solution containing 0.1% gelatin or $5 \cdot 10^{-4}M$ LEO were calculated by applying the modified ILKOVIC equation[6] to the limiting currents of these ions obtained at the RADME (Table I). Table I shows that the apparent values of the diffusion coefficients are almost independent of the drop time, which proves that the maximum of the second kind at the RADME can be completely suppressed by the addition of a suitable amount of the surface-active substance, *e.g.*, 0.1 % gelatin or $5 \cdot 10^{-4}M$ LEO. It can also be seen that the diffusion coefficients in the solution containing 0.1% gelatin are always smaller than those in the solution containing LEO. This result might be explained by assuming that the concentration of reducible ions decreases due to complex formation between reducible ions and gelatin molecules[7].

When the oxidant O is reduced reversibly in the polarographic sense to the reductant R,

$$O + ne \rightleftharpoons R$$

and when the reductant is soluble either in the solution or in the electrode, the current–voltage curve is expressed by the equations:

$$E = E_{1/2} - \frac{0.059}{n} \log \frac{i}{i_l - i} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$E_{1/2} = E_0 - \frac{0.059}{n} \log \frac{k_O}{k_R} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

In eqns. (1) and (2), E_0 is a constant, k_O and k_R are proportionality constants relating the polarographic current and the concentrations of the electroactive substances, and the other terms have their usual meanings. Since the values of k_O and k_R remain constant in the relatively narrow range of the electrode potential where the polarographic wave appears, it is to be expected from eqn. (1) that the relation between E and $\log i/(i_l - i)$ will be a straight line with a reciprocal slope of $0.059/n$ V at 25°. This was experimentally verified with the D.C. current–voltage curve of cadmium ion obtained at the RADME in $0.1M$ potassium nitrate solution containing an insufficient amount of the surface-active substance to suppress the maximum of the second kind. A gradual increase of the reciprocal slope of the log-plot was generally observed when the concentration of gelatin was more than 0.05% (Table II). This might be attributed to the retardation of the electrode reaction at the RADME by the relatively high concentration of gelatin.

The actual value of k_O in eqn. (2) can be experimentally estimated using the relation:

$$k_O = \frac{i_l}{C_O} \quad \ldots\ldots\ldots\ldots \quad (3)$$

where i_l is the limiting current, and C_O is the bulk concentration of the oxidant. In the absence of the "Spüleffekt", the values of k_O and k_R are determined by the drop time, the rate of flow of mercury of the electrode used, and the diffusion coefficients of oxidant and reductant, respectively. The "Spüleffekt" generally increases the values of k_O and k_R. When the reductant dissolves in mercury as in the case of cadmium or lead, the influence of the "Spüleffekt" on k_R can be assumed to be much smaller than that on k_O. In this case, according to eqn. (2), the change of half-wave potential is approximately equal to $0.059/n$ V at 25° when the value of k_O is changed ten times. In our present experiments, the "Spüleffekt" at the RADME does not change the value of k_O more than four times as shown in Tables II and III, and, consequently, it is to be expected that the corresponding change in half-wave potential will be less than $0.036/n$ V. If both the oxidant and reductant diffuse in the same medium as in the case of the trioxalatoferrate(III)–trioxalatoferrate(II) system, it is to be expected that the half-wave potential will not be affected by the "Spüleffekt", because, in such a case, it may be assumed that the influence of the "Spül-

TABLE II

HALF-WAVE POTENTIALS AND RECIPROCAL SLOPES OF LOG-PLOTS OF LEAD, CADMIUM AND TRIOXALATOFERRATE(III) IONS IN THE PRESENCE OF VARIOUS CONCENTRATIONS OF GELATIN

Concn. of gelatin	*Pb(II)*[a]			*Cd(II)*[a]			$Fe(C_2O_4)_3^{-3}$[b]		
%	k_O *µA/mmoles*	$E^{1/2}$ *V vs. S.C.E.*	*Reciprocal slope mV*	k_O *µA/mmoles*	$E^{1/2}$ *V vs. S.C.E.*	*Reciprocal slope mV*	k_O *µA/mmoles*	$E^{1/2}$ *V vs. S.C.E.*	*Reciprocal slope mV*
0	62.98	−0.388	31	52.61	−0.584	30	23.78	−0.240	60
0.005	42.62	−0.384	30	36.62	−0.582	31	16.63	−0.240	58
0.01	31.30	−0.382	31	28.93	−0.578	31	12.01	−0.240	58
0.05	23.67	−0.386	34	22.73	−0.578	33	8.18	−0.248	72
0.1	21.18	−0.390	36	22.70	−0.581	34	6.98	−0.250	72
0.2	18.25	−0.393	36	21.88	−0.582	36	6.83	−0.252	90

[a] In 0.1*M* KNO_3.
[b] In 0.5*M* $K_2C_2O_4$.

TABLE III

EFFECT OF THE HEIGHT OF THE MERCURY COLUMN ON THE HALF-WAVE POTENTIAL OF LEAD AND CADMIUM IONS AT THE RADME IN 0.1*M* KNO_3 SOLUTION CONTAINING NO SURFACE-ACTIVE SUBSTANCES

Height of mercury column cm	$E^{1/2}$ *V vs. S.C.E.*	
	Pb(II)	*Cd(II)*
30	−0.385	−0.582
50	−0.388	−0.584

effekt" on k_O and k_R will be almost the same. The experimental results agreed with this expectation. The half-wave potentials of cadmium, lead and trioxalatóferrate (III) ions at the RADME were found to be practically constant in the concentration range of gelatin, less than 0.01%, where the maximum of the second kind appears on the current–voltage curve (Table II). Table III shows that the half-wave potentials of lead and cadmium ions at the RADME in the solution containing no surface-active substances are almost independent of the height of the mercury column, which also confirms the conclusion that the change of the half-wave potential due to the presence of the "Spüleffekt" is usually negligible in the case of the RADME.

When the concentration of LEO was higher than $2 \cdot 10^{-5} M$, the reduction of lead ion gave typical current–voltage curves similar to those obtained at the conventional DME, but the current–voltage curve of cadmium ion was very much drawn out at the relatively high concentrations of LEO. The limiting currents of lead and cadmium ions at the RADME in $0.1 M$ potassium nitrate solution containing $2 \cdot 10^{-5} M$ LEO were found to be proportional to the concentrations over a wide concentration range (Table IV).

TABLE IV

RELATION BETWEEN THE LIMITING CURRENT, i_l, AT THE RADME AND THE CONCENTRATION OF LEAD OR CADMIUM ION IN $0.1 M$ KNO_3 SOLUTION CONTAINING $2 \cdot 10^{-5} M$ LEO

Concn. of ions (C) *M*	*Pb(II)*		*Cd(II)*	
	i_l[a] μA	i_l/C $\mu A/mmoles$	i_l[b] μA	i_l/C $\mu A/mmoles$
$1.00 \cdot 10^{-3}$	28.58	28.6	26.56	26.6
$5.00 \cdot 10^{-4}$	14.29	28.6	13.24	26.5
$2.00 \cdot 10^{-4}$	5.72	28.6	5.35	26.7
$1.00 \cdot 10^{-4}$	2.85	28.5	2.63	26.3
$5.00 \cdot 10^{-5}$	1.42	28.4	1.34	26.8
$2.50 \cdot 10^{-5}$	0.73	29_2	0.71	28_5
$1.00 \cdot 10^{-5}$	0.29	29_0	0.28	28_0

[a] Measured at —0.47 V *vs.* S.C.E.
[b] Measured at —0.70 V *vs.* S.C.E.

It is concluded from the results mentioned above that the RADME can be used for analytical purposes in D.C. polarography if suitable conditions are selected. The main advantages of the RADME are the reduction of oscillation of the polarographic current during the life of a mercury drop, and the increase in the sensitivity for the limiting current. In D.C. polarography, however, these advantages are partly cancelled by the complicated nature due to the presence of the maximum of the second kind.

A.C. polarography

In A.C. polarography, true peak currents could easily be determined with the RADME at the usual scanning rate of the applied voltage (*e.g.*, 3 mV/sec); this is an important advantage that the RADME has over the conventional DME in routine polarographic analysis.

The effect of the surface-active substance on the height of the peak current of the

A.C. polarogram must be mentioned. Fig. 4 shows the effect of LEO on the peak currents of lead and cadmium ions in 1.0*M* potassium nitrate solution. It was found that the height of the peak current remains practically constant up to a concentration of LEO of $2 \cdot 10^{-5}M$, but decreases with a further increase of the concentration of LEO.

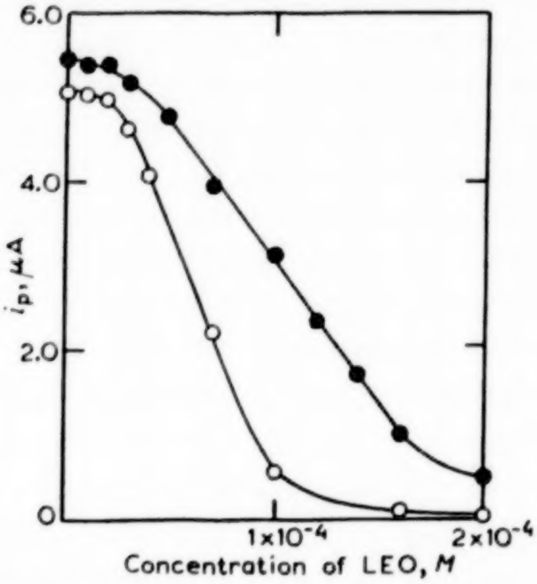

Fig. 4. Effect of the concentration of LEO on the peak currents of $1 \cdot 10^{-4}M$ Pb(II) and Cd(II) ions at the RADME in 1*M* KNO_3 solutions containing $1 \cdot 10^{-3}M$ HNO_3. ●: Pb(II); ○: Cd(II).

Similar phenomena were also observed with the conventional DME, and can be explained by assuming that the electrode reaction is retarded. The experimental results concerning the effect of the surface-active substance indicate that the concentration of the surface-active substance is very critical in A.C. polarographic analysis. In A.C. polarography, it is undoubtedly desirable that the concentration of the surface-active substance should be as low as possible in order to obtain high sensitivity and a reproducible peak current.

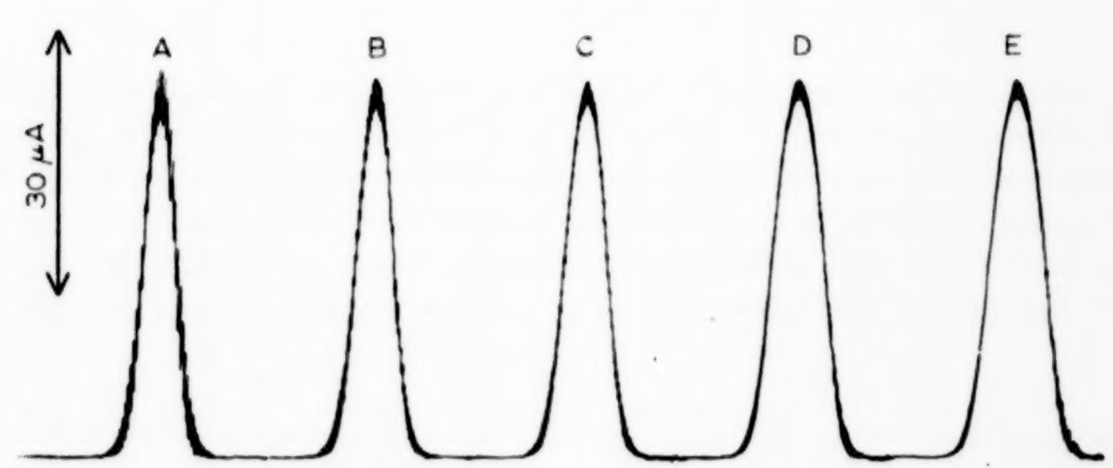

Fig. 5. A.C. polarograms of $8 \cdot 10^{-4}M$ Cd(II) ion obtained at the RADME in 1*M* KNO_3 solution containing $8 \cdot 10^{-6}M$ LEO, at various heights of the mercury column. Height of mercury column: (A) 20 cm; (B) 30 cm; (C) 40 cm; (D) 50 cm; (E) 60 cm.

With such a low concentration of the surface-active substance there exists a "Spüleffekt" at the RADME, as is clearly seen from the D.C. current–voltage curves (Figs. 1, 2 and 3). However, on the basis of theoretical considerations[8] it is to be expected that the A.C. polarographic current will not be affected by the "Spüleffekt"; this was already verified with the rotated dropping mercury electrode applied to A.C. polarography[9]. The influence of the "Spüleffekt" on the A.C. polarographic current was examined by studying the effect of the height of the mercury column on the peak current of cadmium ion in 1.0*M* potassium nitrate solution containing $8 \cdot 10^{-6}M$ LEO (Fig. 5 and Table V). It can be seen that the height of the peak current is independent of the height of the mercury column for heights varying from 20 to 60 cm. This indicates that the influence of the "Spüleffekt" on the peak current is negligibly small as in the case of the rotated dropping mercury electrode.

TABLE V

RELATION BETWEEN THE PEAK CURRENT, i_p, AT THE RADME AND THE HEIGHT OF THE MERCURY COLUMN FOR 0.8 m*M* Cd(II) ION IN 1*M* KNO_3 SOLUTION CONTAINING $8 \cdot 10^{-6}M$ LEO

Height of mercury column	*Drop time*	*Rate of flow of mercury*	*Mean surface area of electrode ($\bar{A}$)*	i_p	$i_p/\bar{A}$
cm	*sec*	*mg/sec*	*cm²*	*μA*	*μA/cm²*
20	1.91	8.72	$3.33 \cdot 10^{-2}$	41.1_0	$12.3_5 \cdot 10^2$
30	1.38	11.97	$3.31 \cdot 10^{-2}$	40.9_2	$12.3_5 \cdot 10^2$
40	0.97	16.8_3	$3.29 \cdot 10^{-2}$	40.8_6	$12.4_1 \cdot 10^2$
50	0.82	20.3	$3.33 \cdot 10^{-2}$	41.1_0	$12.3_5 \cdot 10^2$
60	0.61	27.3	$3.33 \cdot 10^{-2}$	41.1_0	$12.3_5 \cdot 10^2$

The height of the peak current of cadmium ion in the medium mentioned above was found to be proportional to the concentration over the concentration range from $2 \cdot 10^{-5}$ to $1 \cdot 10^{-3}M$. Similar results were also obtained with lead ion in the presence of $2 \cdot 10^{-6}M$ LEO (Table VI). The summit potential, where the peak current was observed, was in agreement with the half-wave potential of the ordinary D.C. polarogram.

TABLE VI

RELATION BETWEEN THE PEAK CURRENT, i_p, AT THE RADME AND THE CONCENTRATIONS OF LEAD AND CADMIUM IONS IN 1*M* KNO_3 SOLUTION

Concn. of ions (C) M	*Pb(II)*[a]		*Cd(II)*[b]	
	i_p *μA*	i_p/C *μA/mmoles*	i_p *μA*	i_p/C *μA/mmoles*
$1.00 \cdot 10^{-8}$	54.6_0	54.6_0	51.6_0	51.6_0
$5.00 \cdot 10^{-4}$	27.3_6	54.7_2	25.8_0	51.6_0
$2.00 \cdot 10^{-4}$	11.1_0	54.6_6	10.3_2	51.6_0
$1.00 \cdot 10^{-4}$	5.4_6	54.6	5.1_6	51.6
$5.00 \cdot 10^{-5}$	2.7_3	54.7	2.5_8	51.6
$2.00 \cdot 10^{-5}$	1.0_8	54.0	1.0_2	51.0

[a] In the presence of $2 \cdot 10^{-6}M$ LEO.
[b] In the presence of $8 \cdot 10^{-6}M$ LEO.

From the experimental results mentioned above, it can be concluded that the RADME gives a reproducible peak current of high sensitivity for the reversible and quasi-reversible electrode reactions. Considering the fact that the A.C. polarographic current is not affected by the presence of the "Spüleffekt", the RADME has a useful advantage over the conventional DME in A.C. polarography, *viz.*, the peak current can be easily and rapidly determined with the usual scanning rate of the applied voltage. Therefore, the use of the RADME is strongly recommended in routine A.C. polarographic analysis.

SUMMARY

The characteristics of the rapidly dropping mercury electrode (RADME) in direct current and alternating current polarography have been investigated. The RADME gives a maximum of the second kind on the D.C. current–voltage curve because of the "Spüleffekt". This maximum is suppressed upon the addition of a large amount of surface-active substance, and typical current–voltage curves similar to those at the DME are obtained. The limiting current at the RADME is proportional to the concentration of the electroactive substance. In A.C. polarography the RADME gives the peak current more accurately than the conventional DME. The height of the peak current is not affected by the "Spüleffekt", and is proportional to the concentration of the electroactive species.

RÉSUMÉ

Les auteurs ont étudié les caractéristiques de l'électrode à goutte de mercure rapide, en polarographie à courant continu et en polarographie à courant alternatif, en donnant des résultats obtenus avec cette électrode. Cette dernière, en polarographie à courant alternatif, présente des avantages sur l'électrode à goutte de mercure ordinaire.

ZUSAMMENFASSUNG

Es wird über Versuchsergebnisse mit der rasch-tropfenden Quecksilberelektrode bei der Gleichstrom- und Wechselstrom-Polarographie berichtet. Mit der rasch-tropfenden Quecksilberelektrode werden bei der Wechselstrom-Polarographie bessere Werte erhalten als mit der üblichen Quecksilbertropfelektrode.

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COULOMETRIC TITRATION WITH ELECTROGENERATED +2 TIN

TITRATION OF +3 GOLD AND +5 VANADIUM

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In a recent study[1] in this laboratory the conditions under which +2 tin can be electrogenerated with 100% current efficiency have been determined. Iodine and bromine can be titrated successfully by use of either a gold or platinum generator electrode provided a concentrated (3 to 4*M*) bromide solution of stannic chloride is used as supporting electrolyte. The titration of iodine serves for the determination of substances which oxidize iodide ion to iodine (coulometric iodometry) and the bromine titration can be employed for the determination of those organic compounds that undergo bromination or oxidation by bromine.

The present study extends the applications of coulometric titration with +2 tin to the determination of +3 gold and +5 vanadium. Although these elements can be titrated iodometrically, the direct titrations are more selective and subject to fewer interferences.

A coulometric titration of +3 gold to the elemental state in a hydrochloric acid medium with electrogenerated chlorocuprous ion, using potentiometric e.p. indication, has been described by LINGANE[2]. The titration with +2 tin was performed using potentiometric, amperometric, and spectrophotometric end-points.

The titration of +5 vanadium has been performed previously with several coulometric reductants. With chlorocuprous ion[3], or ferrous ion[4], reduction of vanadium proceeds to the +4 state, while titanous ion[5] causes reduction to +3 vanadium. With +2 tin the titration of +5 vanadium proceeds to the +4 state, and the e.p. can be recognized potentiometrically.

EXPERIMENTAL

The titration cell, apparatus, and conditions for 100% current efficiency have been described previously[1]. Amperometric and potentiometric e.p. detection followed the usual practice[6].

Absorption curves were recorded with a Cary Recording Spectrophotometer, Model 11 (Applied Physics Corp., Pasadena, Calif.). Spectrophotometric titrations were performed in a 180 ml tall form beaker held in a modified cell-holder of a Beckman DU Spectrophotometer. The generator electrode and the auxiliary electrode chamber were introduced into the cell through a stopper, from above, in such a manner as to be out of the light path. The solution was stirred by means of a magnetic stirrer beneath the cell compartment.

The optimum supporting electrolyte is 3 to 4*M* sodium bromide, 0.3*N* hydrochloric acid, and 0.2*M* stannic chloride. As discussed in a previous paper[1], with this electrolyte current efficiency for reduction of +4 tin remains at 99.5 to 99.9% with generating current densities of 10 to 84 mA/cm^2 at a gold generator cathode.

PERFORMANCE DATA

Titration of gold

The general characteristics of the potentiometric titration curve of +3 gold are

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shown by the automatically recorded curve in Fig. 1. The main inflection occurs after the equivalence point chiefly because the reaction is somewhat slow near the e.p. When the titration is performed manually, with 1 to 2 min waiting periods between each generation increment, the inflection coincides with the e.p.

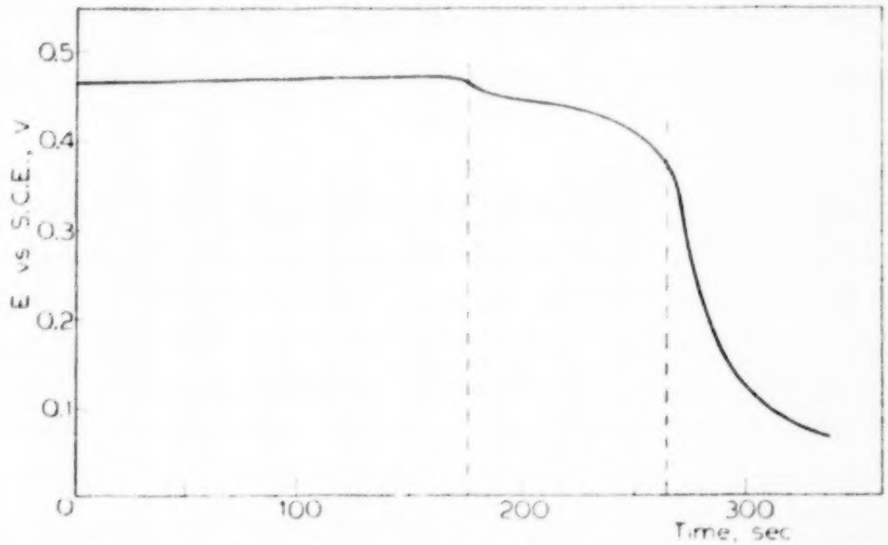

Fig. 1. Titration of 5.58 mg of +3 gold in 70 ml of $4M$ sodium bromide, $0.2M$ stannic chloride, and $0.3N$ hydrochloric acid, with a generating current of 31.1 mA. The potential of a gold indicator electrode during the titration was recorded automatically with a recording potentiometer.

It is evident from the first small inflection that the reduction of $AuBr_4^-$ proceeds stepwise, first to $AuBr_2^-$ and finally to the metal. Just as in the titration of +3 gold with chloro cuprous ion in chloride medium[2], the potential of the gold indicator electrode increases slightly, but definitely, during the first two thirds of the titration. This anomaly, which persists even in manual titrations with several min waiting at each point, results from the fact that a gold electrode is very slow in acquiring its equilibrium potential in a solution containing a mixture of +3 and +1 gold. The increase in potential is considerably smaller than was previously observed[2] in chloride medium, which suggests that the $AuBr_4^-/AuBr_2^-$ couple behaves somewhat more reversibly than does the $AuCl_4^-/AuCl_2^-$ couple. This same anomalous increase in potential has also been observed by ERDEY AND RADY[7] in their recent study of the titration of +3 gold with ascorbic acid in the ordinary volumetric manner.

During the last third of the titration the potential stabilizes rapidly and its value corresponds closely to the value expected from the standard potential of the $AuBr_2^-$/Au couple.

Accurate measurements of the standard potentials of the three gold couples in bromide media do not appear to have been made at 25°. However, from the measurements of GRUBE *et al.*[8] at 60°

$$AuBr_2^- + e = Au + 2Br^-;\ E^\circ = 0.96\ \text{V}\ vs.\ \text{N.H.E.}$$

$$AuBr_4^- + 3e = Au + 4\ Br^-;\ E^\circ = 0.87\ \text{V}\ vs.\ \text{N.H.E.}$$

$$AuBr_4^- + 2e = AuBr_2^- + 2Br^-;\ E^\circ = 0.82\ \text{V}\ vs.\ \text{N.H.E.}$$

From these values, we have for the disproportionation equilibrium at 60°

$$3AuBr_2^- = 3Au + AuBr_4^- + 2Br^-$$

$$K = \frac{(AuBr_4^-)(Br^-)^2}{(AuBr_2^-)^3} = 54000$$

From the magnitude and form of this equilibrium constant it is clear, with a large total concentration of $AuBr_2^-$ and $AuBr_4^-$, and a relatively small concentration of bromide ion, that +1 gold is unstable. However, under the diametrically opposite conditions of the present study (very small total concentration of gold and very large bromide ion concentration) the balance of the disproportionation equilibrium should be far to the left. The observed stepwise reduction of the +3 gold is consistent with this prediction.

The titration can also be followed amperometrically by observing the current between two identical, small gold electrodes (1 cm² each is suitable) across which a constant voltage of the order of 100 to 200 mV is impressed. Fig. 2 shows a typical amperometric titration curve. The anode is depolarized throughout the titration by the reaction $Au + 2Br^- = AuBr_2^- + e$, and the cathode, at which the reaction is initially $AuBr_4^- + 2e = AuBr_2^- + 2Br^-$ and finally $AuBr_2^- + e = Au + 2Br^-$, actually functions as the indicator electrode. The indicator current decreases continuously up to the e.p. in tune with the decreasing concentrations of $AuBr_4^-$ and $AuBr_2^-$. The irreversible behaviour of the stannic–stannous couple causes the indicator current to remain very small beyond the e.p. There is some semblance of an increase in slope at the two-thirds point, which suggests that the overpotential required for

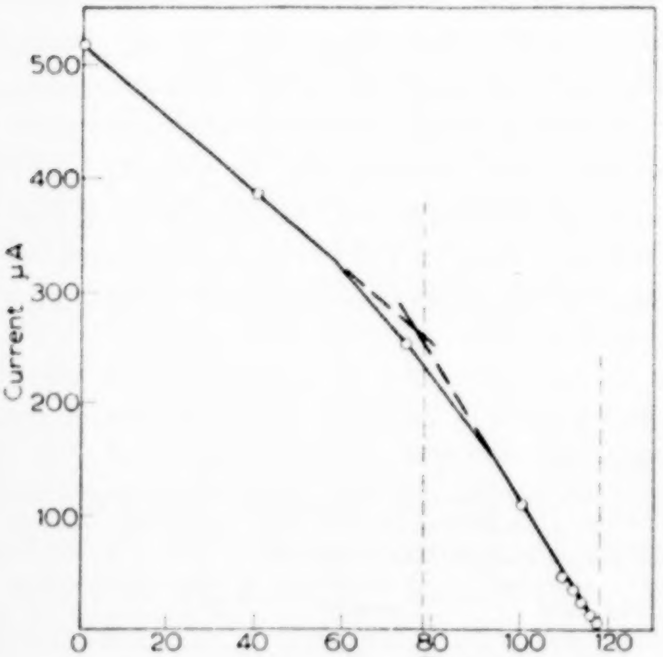

Fig. 2. Amperometric titration of 5.27 mg of +3 gold in 70 ml of 4*M* sodium bromide, 0.2*M* stannic chloride, and 0.3*N* hydrochloric acid, with a generating current of 64.9 mA. A constant voltage of 150 mV was impressed across the two indentical gold indicator electrodes (area 1 cm² each).

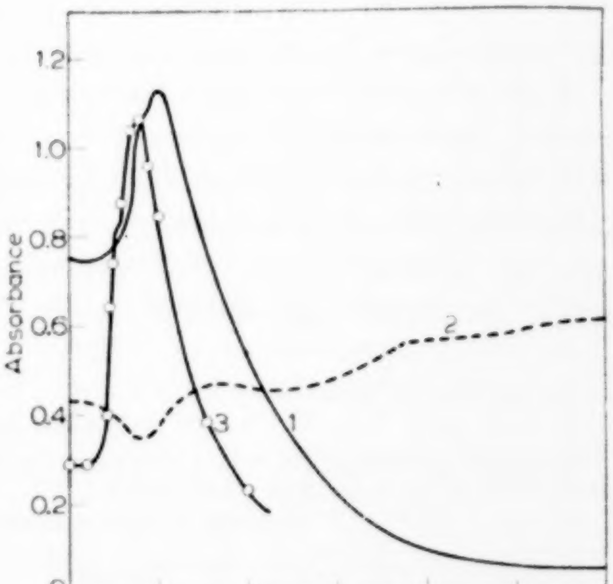

Fig. 3. Absorption spectra during the titration of 100 ml of 0.346 m*M* +3 gold in 4*M* sodium bromide, 0.2*M* stannic chloride, and 0.25*M* hydrochloric acid. (1) Original solution. (2) Solution titrated past the two-thirds point, containing $AuBr_2^-$ and colloidal gold. (3) 0.402 m*M* +2 tin alone. Curves 1 and 2 were recorded with a 1-cm light path, but a 10-cm light path was used for curve 3.

the reduction of $AuBr_2^-$ is smaller than that for the reduction of $AuBr_4^-$, but obviously this e.p. is too indistinct for practical use.

During the titration of $AuBr_4^-$ with +2 tin, the solution, initially colored orange-yellow, changes to colorless when the titration is two-thirds complete, and then to various shades of purple as colloidal gold is formed. These color changes suggested the possibility of following the titration spectrophotometrically.

Fig. 3 shows spectrophotometric absorption curves taken during a titration of +3 gold with electrogenerated +2 tin. The absorption peak of $AuBr_4^-$ at 400 mμ has an extinction coefficient of 3,270 l/mole cm. TURKEVICH *et al.*[9] found that colloidal gold sols, in the presence of aurous gold, show a broad absorption band throughout the visible region, rising to a maximum at about 700 mμ. Curve 2 corresponds to this description. From curve 3 it is seen that $SnBr_4^{-2}$ has an absorption peak at about 388 mμ (depending slightly upon the tin concentration) with an extinction coefficient of only 268 l/mole cm. The stannic bromide complex absorbs only in the region of 300 to 360 mμ with a maximum at about 320 mμ.

The spectrophotometric titration of +3 gold was performed by setting the Beckman DU spectrophotometer at a wave-length of 400 mμ, the slit width at 0.15 mm, and the absorbance at 0.00 with the cell removed from the holder. The use of air as reference (zero absorbance) is convenient, since only the change in absorbance rather than its absolute value is needed for titration purposes.

A typical spectrophotometric titration curve is shown in Fig. 4. The absorbance readings were independent of the stirring rate, and became stable within 1 min. After the e.p. (reduction of +3 to +1 gold) the readings took about 15 min to become fairly steady, because the gold sol was undergoing particle size (and absorption) fluctuations. In contradistinction to potentiometric and amperometric detection, spectrophotometric detection reveals only the first e.p. and the second is inaccessible.

Table I summarizes data obtained in 37 titrations using potentiometric, amperometric, and spectrophotometric e.p. detection. In each case the supporting electrolyte was pre-titrated to the e.p. before the gold sample was added. With either potentiometric or amperometric detection 0.5 to 23 mg of gold is titratable with an average error of *ca.* ± 0.3%. Spectrophotometric titration was both less precise and less accurate (average error *ca.* + 2%).

TABLE I

COULOMETRIC TITRATION OF +3 GOLD

Supporting electrolyte was $4M$ sodium bromide, $0.2M$ stannic chloride, and $0.3N$ hydrochloric acid, and the volume was 70 to 110 ml. The area of the gold generator cathode was 1 cm², except with the 22.62 mg sample, in which case it was 4 cm².

Gold taken mg	*No. of trials*	*Current mA mg*	*Gold found (average) mg*	*Average deviation mg*	*End-point detection*
5.271	5	63.90	5.259	±0.015	Potent.
5.271	4	32.14	5.276	±0.018	
1.055	3	9.971	1.055	±0.001	
22.62	4	100.75	22.76	±0.04	Amp.
5.271	7	65.00	5.266	±0.012	
5.271	6	34.10	5.272	±0.009	
5.271	3	9.961	5.271	±0.007	
5.271	4	60.75	5.370	±0.069	Spectro.
5.271	1	33.36	5.267	—	

We have not investigated interference by other metals. However, of the elements commonly associated with gold, we would not expect interference from lead, silver or mercury. Quite possibly platinum may interfere as it does in the titration with chloro cuprous ion in chloride medium[2].

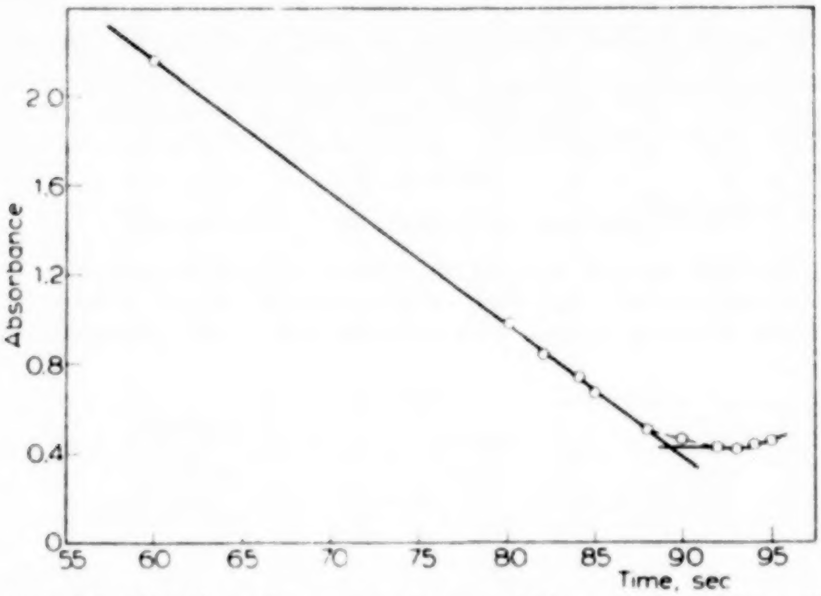

Fig. 4. Spectrophotometric titration of 5.27 mg of +3 gold in 100 ml of 4*M* sodium bromide, 0.2*M* stannic chloride, and 0.3*N* hydrochloric acid, with a generating current of 60.7 mA. Absorbance was measured against air at 400 mμ. The end-point corresponds to reduction of the +3 gold to the +1 state.

Titration of +5 vanadium

The titration of +5 vanadium to the +4 state was performed with the same supporting electrolyte used for the titration of gold, using potentiometric e.p. detection. Amperometric e.p. detection is not suitable because in acidic bromide medium the V^{+5}–V^{+4} couple behaves irreversibly, and since the stannic–stannous couple also functions irreversibly there is no clear definition of an end-point.

The titration can also be followed spectrophotometrically by measuring the change in absorbance at 390 mμ. At this wave length +5 vanadium and +2 tin both absorb strongly, whereas +4 vanadium and +4 tin do not. Hence the titration curve is V-shaped with the e.p. at minimum absorbance.

In the acidic bromide medium used (4*M* sodium bromide, 0.25*N* hydrochloric acid, and 0.2*M* stannic chloride) the formal potential of the V^{+5}/V^{+4} couple is +0.63 V *vs.* S.C.E. (+0.87 V *vs.* N.H.E.). This is large enough, in the presence of a high concentration of bromide ion, so that some of the +5 vanadium is reduced by bromide ion when the sample is added to the supporting electrolyte. Because the bromine formed is partly lost by volatilization in the nitrogen stream used to remove dissolved air, this reaction causes a negative error.

For example, when eight 2.739-mg samples of +5 vanadium were titrated one after the other in the same batch of supporting electrolyte the errors in percent were *seriatim* —7.9, —5.1, —2.1, +0.3, 0.0, —0.4, —0.4, and —0.5. The negative error, initially quite large, disappeared after three samples were added and titrated. The reason for this effect is that +4 vanadium accumulates in the solution during the successive titrations, and after about three samples have been titrated (*i.e.*, when the concentration ratio of +5 to +4 vanadium becomes 1/3 or smaller) the potential of the V^{+5}/V^{+4} couple is decreased sufficiently so that +5 vanadium no longer oxidizes bromide ion.

The obvious way to prevent this error in the first place is to add to the supporting electrolyte sufficient +4 vanadium (as vanadyl sulfate) so that the potential of the V^{+5}/V^{+4} couple is kept below the value at which bromide ion is oxidized. This was done in all subsequent titrations. In addition the supporting electrolyte (containing +4 vanadium) was pre-titrated to the e.p. before the sample of +5 vanadium was added.

TABLE II

COULOMETRIC TITRATION OF +5 VANADIUM

The supporting electrolyte was $4M$ sodium bromide, $0.2M$ stannic chloride, $0.25N$ hydrochloric acid, and $0.004M$ vanadyl sulfate, and the volume was *ca.* 70 ml. Dissolved air was removed with nitrogen. The area of the gold generator cathode was 1 cm^2. Potentiometric e.p. detection was employed.

Vanadium taken mg	*No. of trials*	*Current mA*	*Vanadium found (average) mg*	*Average deviation mg*
2.739	5	34.56	2.738	±0.002
2.739	5	34.46	2.738	±0.007
5.467	3	67.08	5.472	±0.010
5.467	4	68.50	5.461	±0.004
0.5462	7	10.48	0.5458[a]	±0.0046

[a] In these trials +2 tin was generated beyond the e.p. and the excess was back titrated with electrogenerated bromine using a 1-cm^2 platinum anode.

Results obtained in 24 titrations of 0.5 to 5.5 mg quantities of +5 vanadium are summarized in Table II. The average deviation is seen to be *ca.* ±0.2% with the larger samples and ±0.8% with the 0.5 mg samples.

ACKNOWLEDGEMENT

Appreciation is expressed to the National Science Foundation for a fellowship held by one of us (A.J.B.).

SUMMARY

Methods are described for the titration of +3 gold and +5 vanadium with electrogenerated +2 tin in an acidic bromide medium. Quantities of gold from 1 to 23 mg are titratable with an average error of *ca.* +0.3%, using either potentiometric or amperometric e.p. detection. Spectrophotometric detection can also be used but is somewhat less precise, Using potentiometric detection 0.5 to mg of +5 vanadium is titratable to the +4 state with an average error of ±0.2%.

RÉSUMÉ

On décrit des méthodes pour le titrage coulométrique de l'or(III) et du vanadium (V) au moyen de l'étain(II), en solution acide, en présence de bromure, avec détection potentiométrique, ampérométrique ou photométrique du point final.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur coulometrischen Titration von Gold-(III) und Vanadium-

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(V) mit Hilfe von Zinn-(II) in bromidhaltiger, saurer Lösung. Der Endpunkt kann potentiometrisch, amperometrisch oder photometrisch bestimmt werden.

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THE DETERMINATION OF SILVER IN GALENA AND BLENDE BY RADIOACTIVATION ANALYSIS

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The abundance of silver in the igneous rocks of the crust of the earth is low, apparently *ca.* $10^{-6}\%$. The element is familiar however, due to its concentration in workable deposits and because it possesses desirable properties which have promoted production for many centuries. Much silver is extracted from ores of other metals, and the minerals galena and blende make a considerable contribution to silver production. The determination of silver in such minerals is therefore of economic importance. Moreover, from a geological standpoint accurate information on the distribution of a trace element such as silver may throw light on the origin of ore deposits.

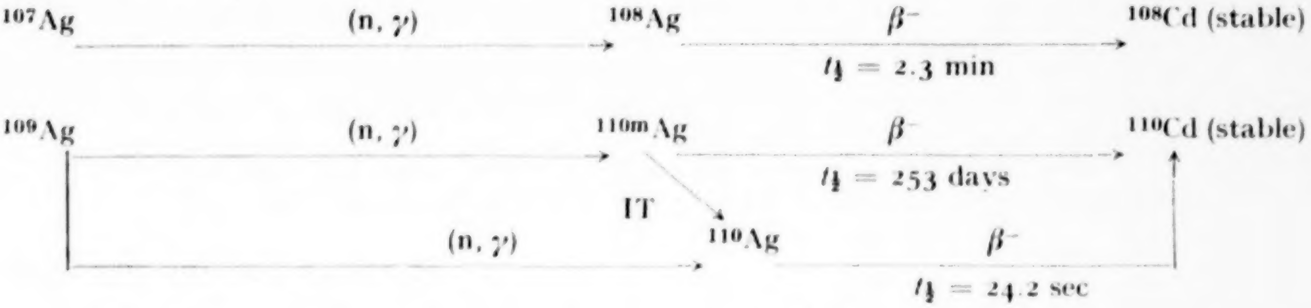
In the present paper the determination of traces of silver in galena and blende by neutron-activation analysis is described. Neutron-activation analysis has the advantage of high sensitivity for many elements, and can generally be made specific for a given element. The possibility of using carriers in radiochemical separations avoids the difficulties of chemical operations with ultra-micro quantities, such as problems of coprecipitation, adsorption, and reagent blanks. The accuracy attainable by radioactivation analysis is also often better than that obtained by spectrochemical analysis.

A comprehensive bibliography on analyses of trace elements in galena and blende up to 1955 is provided in a review by Fleischer[1]. A recent extensive study, utilizing the catbode-layer carbon arc spectrochemical method of analysis, has been made by El Shazly, Webb and Williams[2].

The principles, applicability, and limitations of radioactivation analysis have been extensively reviewed elsewhere[3-7], and will not be dealt with here.

RADIOACTIVATION OF SILVER

Silver has two stable isotopes ^{107}Ag (% abundance 51.35) and ^{109}Ag (% abundance 48.65), which on irradiation with thermal neutrons undergo nuclear reactions of the following type:



The thermal neutron activation cross sections for the stable silver isotopes are[8]:

^{107}Ag (n, γ)^{108}Ag $\sigma = 44$ barns
^{109}Ag (n, γ)^{110m}Ag $\sigma = 2.8$
^{109}Ag (n, γ)^{110}Ag $\sigma = 110$

and a summary of nuclear data for the different radioisotopes of silver produced in the nuclear reactions is given in Table I[9,10].

TABLE I

SUMMARY OF NUCLEAR DATA FOR SOME RADIOISOTOPES OF SILVER

Radioisotope	*Half-life*	*Radiations and energies, MeV*
^{108}Ag	2.3 min	β 1.77; (EC; γ 0.43, 0.60; β^+)
^{110m}Ag and ^{110}Ag	253 days	β 0.530 (35%), 0.087 (58%), 2.12 (3%), 2.86 (3%); γ 0.116 to 1.51
^{110}Ag	24.2 sec	β 2.16 (60%), 2.84 (40%); γ 0.66, 0.94 (weak), others.

It has been estimated by JENKINS AND SMALES[7] that, with irradiation at a flux of 10^{12} neutrons/cm^2/sec for one month, the ultimate sensitivity for silver when the activity of the radionuclides ^{110m}Ag–^{110}Ag is measured is $5 \cdot 10^{-9}$ g. Utilizing the neutron flux available in the Harwell nuclear reactor BEPO, *ca.* 10^{12} neutrons/cm^2/sec, it follows that the silver in small samples of galena and blende may easily be determined. A procedure involving the chemical separation and radiometric assay of the radionuclides ^{110m}Ag–^{110}Ag from neutron irradiated samples is described in this paper.

If facilities had been available for counting the samples shortly after neutron irradiation, it may have been possible, using the 2.3 min radio nuclide ^{108}Ag, to determine the silver content of some galena specimens without any chemical separation being required[11,12].

ANALYSIS METHOD

Preparation of the mineral specimens for analysis

The specimens analyzed were of good quality, and separations employing heavy liquids or magnetic methods appeared to be unnecessary. Small apparently homogeneous crystals of the minerals were examined under high magnification and separated by hand-picking. These were ground to a fine powder in an agate mortar, with the usual precautions as to the avoidance of contamination. Samples consisting of *ca.* 0.3 g of powdered mineral were weighed out accurately into irradiation containers made from 4-mm internal diameter silica tubing, which were then sealed.

Neutron irradiation of samples and standards

In order to avoid self-shielding differences with samples and standards[6], standards were prepared by adding known small quantities of silver to mineral specimens to be analyzed. This was done by adding aliquot portions of a dilute standard solution of silver, and a drop of wetting-agent, to 0.3 g samples of powdered mineral in 4 mm internal diameter silica irradiation tubes. The liquid in the tubes was allowed to soak into the mineral powder, and then was carefully evaporated to dryness, after which the tubes were sealed.

Standards containing the added silver and some samples of minerals of unknown silver content together with samples to which no silver had been added, were packed with glass wool into a standard 7.5 cm × 2.5 cm aluminium can for irradiation in BEPO. Irradiation was usually for 2–3 days. On delivery from Harwell after irradiation, the samples and standards were analyzed radiochemically for ^{110m}Ag–^{110}Ag by the procedure described below.

Chemical separation

MEINKE AND ANDERSON[11] have studied the determination of silver by radioactivation analysis with a low-flux neutron source (25 mg Ra–Be) and measurement of the activity of ^{108}Ag. Samples were counted without chemical treatment. SMALES[13] has determined silver in a sodium–potassium alloy using ^{110m}Ag also without chemical separation, but utilizing γ-scintillation spectrometry.

Various procedures involving carriers and "scavenging precipitations" have been described for the separation of silver activity, *e.g.* the separation from cyclotron targets[14] and fission product mixtures[15–17], and in the radioactivation analysis of sodium-potassium alloy[18]. SUNDERMAN AND MEINKE[19] have also investigated the radiochemical separation of silver on the basis of an evaluation of precipitation, electrodeposition, and isotopic exchange procedures. However, no radiochemical methods appear to have been published for isolating silver activity from irradiated minerals. In the present work, carrier chemistry and a series of scavenging precipitations have been used to secure the necessary separation of silver from a large number of other elements. The irradiated mineral samples and standards have been dissolved in nitric acid. Silver has been initially separated by precipitation of the chloride from the nitric acid solution. The silver then has been purified by ferric hydroxide scavenging and silver sulphide precipitation, both performed in ammoniacal solution. After repetition of the above cycle, the silver has been converted to the oxide and finally to the iodate $AgIO_3$, in which form it has been counted. Chemical yields of 50% or better have always been obtained.

Reagents

Ag carrier: 10 mg Ag/ml (added as $AgNO_3$ in very dilute HNO_3) standardized; Tl^{I} carrier: 10 mg Tl/ml (added as $TlNO_3$ in very dilute HNO_3); Fe^{III} carrier: 10 mg Fe/ml (added as $FeCl_3$.

$6H_2O$ in very dilute HCl); *N* HCl; 6*N* HCl; 6*N* HNO_3; conc. HNO_3; conc. H_2SO_4; KIO_3, saturated solution; 6*N* NaOH; conc. NH_4OH; $(NH_4)_2S$, saturated solution; Manoxol OT, 0.1% in water; 95% ethyl alcohol.

Preparation and standardization of carrier

Dissolve 15.75 g of $AgNO_3$ in a minimum amount of H_2O, add a few drops of HNO_3, and dilute the solution to 1 l.

Pipette exactly 5 ml of the carrier solution into a 50-ml centrifuge tube and dilute to 20 ml with H_2O. Add 1 ml of saturated KIO_3 solution and stir to coagulate the precipitate which forms. Add an additional drop of KIO_3 to test for completeness of precipitation. Filter the precipitate into a weighed sintered glass crucible of grade 3 or 4. Wash the precipitate with 5 ml of 95% ethyl alcohol and dry in an oven at 110° for 15 min. Cool and weigh as $AgIO_3$.

Radiochemical separation procedure

Step 1. Remove the silica tubes from the can, open them at the constriction, and transfer the solid samples to 50-ml centrifuge tubes. Wash out the tubes with a little warm dil. HNO_3 and transfer the washings quantitatively to the centrifuge tubes (a).

Step 2. To a sample in a 50-ml centrifuge tube add 2 ml of standard Ag carrier and 2 ml Tl^I carrier. Add 4 ml conc. HNO_3 and dissolve the sample by boiling the solution. Add a further 5 ml of conc. HNO_3 and boil for 10 min. Dilute to 40 ml, centrifuge, and discard any precipitate of sulphur.

Step 3. Add a few drops of Manoxol OT solution and heat to boiling (b). Add 6*N* HCl drop by drop until precipitation of AgCl is complete. Heat until the AgCl has coagulated. Centrifuge and discard the supernate.

Step 4. Wash the precipitate three times with 10 ml portions of boiling H_2O. Dissolve the AgCl in 2 ml conc. NH_4OH (c). Dilute to 20 ml with H_2O and add 1 ml of Fe^{III} carrier. Centrifuge, transfer the supernate to a clean 50-ml centrifuge tube, and discard the precipitate.

Step 5. To the solution add 1 ml of saturated $(NH_4)_2S$ solution. Stir vigorously and centrifuge. Discard the supernate.

Step 6. Dissolve the Ag_2S precipitate by heating with 1 ml of conc. HNO_3. Dilute to 20 ml with H_2O and precipitate AgCl as in step 3.

Step 7. Repeat steps 4 and 5.

Step 8. Dissolve the Ag_2S precipitate by heating with 1 ml of conc. HNO_3. Make the solution alkaline with 6*N* NaOH, and add 3 drops in excess. Centrifuge the Ag_2O precipitate and discard the supernate. Dissolve the Ag_2O in 4 drops of conc. H_2SO_4 and evaporate completely to dryness (d). Cool.

Step 9. Dissolve the residue in 20 ml of distilled H_2O and add 1 ml of saturated KIO_3 solution. Centrifuge and discard the supernate.

Step 10. Dissolve the $AgIO_3$ precipitate in 4 drops of conc. NH_4OH. Centrifuge, transfer the supernate to a clean 50-ml centrifuge tube. Centrifuge and discard any S residue.

Step 11. Add 3 drops of conc. H_2SO_4 to the solution. Centrifuge the $AgIO_3$ precipitate and wash twice with water and once with 5 ml of 95% ethyl alcohol. The precipitate is then ready to be mounted for counting.

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Notes

(a) It is essential that steps 1 and 2 be carried out in an efficient fume-cupboard.

(b) The addition of Manoxol OT helps to coagulate the AgCl and to prevent its adherence to the walls of the tube.

(c) A little heating may be necessary.

(d) It is not necessary to remove the last traces of H_2SO_4 on the walls of the tube.

Mounting and counting of the $AgIO_3$ precipitate

Slurry the washed $AgIO_3$ precipitate from step 11 of the radiochemical separation procedure with 95% ethyl alcohol onto a weighed aluminium counting tray (A.E.R.E. cat. no. 4-3/1068), by using a transfer pipette. Make sure the distribution of the precipitate on the tray is uniform. Dry at 110° for 15 min and weigh to establish the chemical yield (20 mg Ag $\equiv$ 52.43 mg $AgIO_3$).

To avoid any self-absorption differences, the weights of $AgIO_3$ mounted from different samples should preferably be similar. It has been demonstrated, however, by measuring the activity of a given amount of $^{110m}Ag-^{110}Ag$ with different weights of $AgIO_3$, that no correction for self-absorption needs to be made for the range of weights of $AgIO_3$ obtained by the radiochemical procedure.

In the present work the final precipitates of $AgIO_3$ were counted under a thin end-window Geiger-Müller counter (EHM 2/5), with conventional associated electronic equipment. A statistical accuracy of 0.5% was achieved by measuring a total of 40,000 counts where possible. When the activity was low, counting was carried out for a period of 40 min. All measured activities were corrected for paralysis, background, and chemical yield.

In order to check for radiochemical purity, standard aluminium absorption curves of samples were measured[20] and compared with curves from $^{110m}Ag-^{110}Ag$ tracer supplied by the Radiochemical Centre, Amersham, which had been put through the radiochemical separation procedure described above. Typical results are shown Fig. 1.

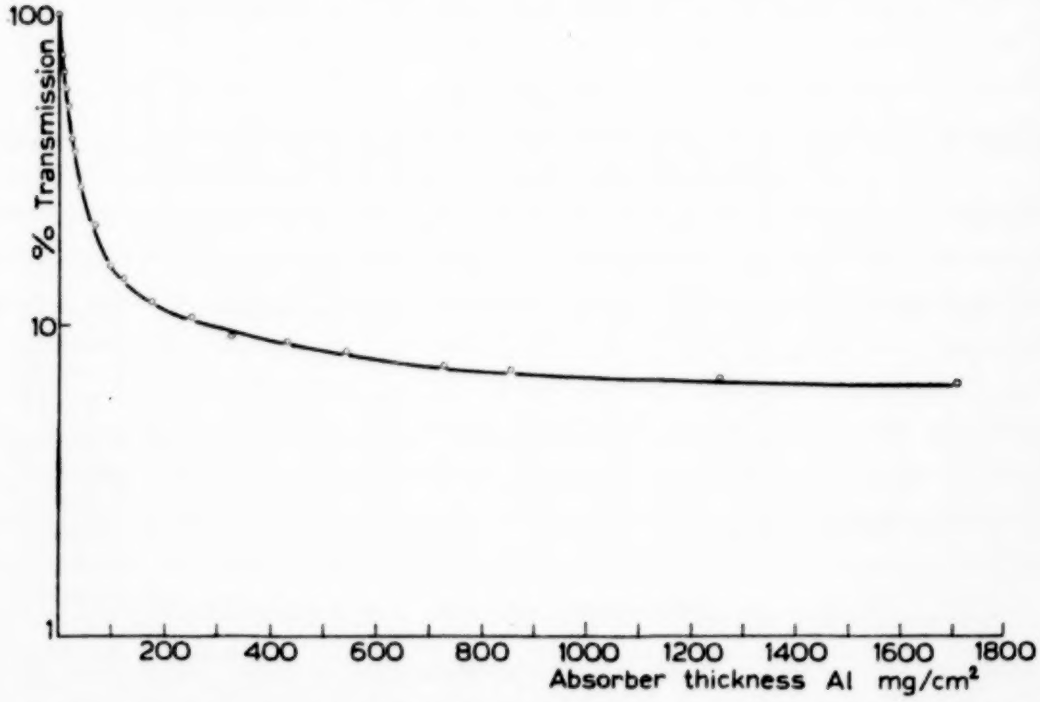

Fig. 1. Aluminium absorption curve of $^{110m}Ag-^{110}Ag$. The full curve is for purified silver tracer, while the recorded points are for a final precipitate from an analysis sample.

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In addition, decay curves measured for a period of a few weeks corresponded satisfactorily with the published half-life of ^{110m}Ag.

To confirm that there was no trace of thallium contamination in the silver procedure, tracer tests were made using carrier-free 4.1 year ^{204}Tl (supplied by the Radiochemical Centre, Amersham). Aliquots of the tracer solution containing $> 300{,}000$ counts/min of ^{204}Tl were taken for the tests of the silver procedure. In two experiments the $AgIO_3$ precipitates at the end of the procedure contained no detectable activity above the background for the counter.

From the above work it is evident that the silver procedure provides satisfactory radiochemical purity.

RESULTS

If A_1 is the silver activity (corrected for paralysis, background, and chemical yield) for a standard containing w μg of added Ag, and A_2 is the corrected activity of a corresponding sample of the same weight but with no added Ag, it follows that an

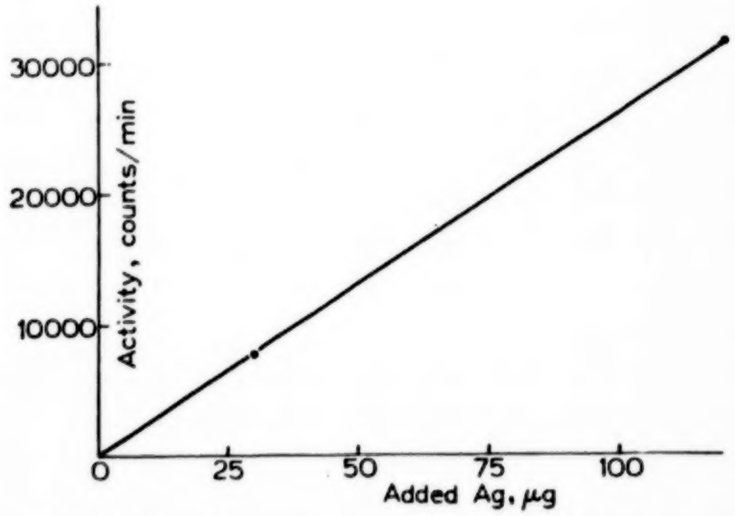

Fig. 2. Activity due to added silver in neutron irradiated standards plotted against weight of added silver. Each point is the mean of two measurements.

TABLE II

SILVER CONTENT OF GALENA AND BLENDE FROM MILLTOWN MINE, TULLA, CO. CLARE, EIRE, DETERMINED BY NEUTRON-ACTIVATION ANALYSIS

Galena		*Blende*	
Specimen 1G	0.105 %	Specimen 1B	0.00075 %
	0.104		0.00074
	0.104		0.00078
	0.105		0.00078
	0.102		0.00074
	0.102		0.00076
			0.00075
mean	0.104		0.00073
			0.00074
			0.00077
Specimen 2G	0.110		
	0.109	mean	0.00075
mean	0.110		

activity of A_1—A_2 corresponds to *w* μg Ag. The silver content of samples may therefore be calculated from their corrected counting rates.

Fig. 2 shows a typical graph of corrected activity due to added silver in a series of standards plotted against the weight of added silver. The fact that graphs of this type are straight lines passing through the origin indicates that the standards are satisfactory, and that no "blank correction" needs to be made for silver in the conductivity water with which the standard solutions of silver were made.

Typical analysis results obtained by the radioactivation method are shown in Table II. These refer to samples of associated galena and blende from Milltown Mine, Tulla, Co. Clare, Eire. The results show that in this case there is a marked tendency for silver to concentrate in galena rather than in blende. This is in agreement with "size considerations" (ionic radii: Ag^+ 1.26 Å, Pb^{+2} 1.20 Å, Zn^{+2} 0.69 Å), which suggest that silver is more likely to undergo isomorphous substitution for lead than for zinc in minerals.

DISCUSSION

The method described in this paper may be applied to samples containing $< 0.0001\%$ silver, and the ultimate sensitivity of the method may easily be increased by lengthening the time of neutron irradiation. Conventional spectrochemical methods of analysis have a limiting sensitivity of *ca.* 0.0001% Ag[2]. Thus the radioactivation method of analysis has the advantage of better sensitivity, and also avoids various errors inherent in emission spectroscopy.

Precision (standard deviation) of the radioactivation analyses has always been better than ± 3%.

The method described in this paper should be applicable to various minerals other than galena and blende, although in some cases the need may arise for some modification of the radiochemical separation procedure.

In the neutron-activation analysis of silver in minerals, allowance must be made for the fact that elements other than silver undergo nuclear reactions leading to the formation of silver isotopes. Possible secondary reactions of this type are ^{110}Cd (n, p)^{110m}Ag and ^{113}In (n, α)^{110m}Ag, whereby $^{110m}Ag-^{110}Ag$ activity is produced from cadmium and indium. These nuclear reactions may occur with fast neutrons (of which there is a proportion in BEPO, possibly *ca.* 10% of the slow neutron flux in the case of irradiations used in the present work).

An estimate of possible interference has been made by irradiating samples of pure CdO and In_2O_3, together with pure $AgNO_3$ standards, in the Pile for 1 week. The silver activity was separated and counted as before. The experimental results showed that if a mineral contained 1% of cadmium this might give rise to a maximum spurious silver content of 0.02 p.p.m. Similarly an indium content of 0.1% could give rise to a limiting spurious silver content of 0.002 p.p.m. Such interferences are sufficiently small to be ignored in the analysis of silver in galena and blende.

Any interference of importance due to the production of radioisotopes of silver other than $^{110m}Ag-^{110}Ag$ would have been apparent from energy measurements made on the counted samples from mineral specimens.

ACKNOWLEDGEMENTS

Thanks are due to Mr. P. G. EMBREY and Dr. J. R. BUTLER for kindly providing mineral specimens.

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SUMMARY

Neutron-activation analysis has been applied to the determination of traces of silver in specimens of galena and blende. Use has been made of the radionuclides ^{110m}Ag–^{110}Ag. The radiochemical separation after the addition of carrier has been based mainly on precipitations of silver as chloride, sulphide, oxide, and iodate. Radiochemically pure silver was finally precipitated and counted as the iodate; the chemical yield was determined gravimetrically. In order to avoid errors due to self-shielding, standards were made by adding small known amounts of silver to analytical samples. Precision (standard deviation) of the radioactivation analyses has been better than ± 3% in all cases.

RÉSUMÉ

On propose une méthode de dosage de l'argent, à l'état de trace, dans une galène ou dans une blende, par activation au moyen de neutrons. La séparation radiochimique après addition d'entraîneur est basée principalement sur les précipitations de l'argent comme chlorure, sulfure, oxyde et iodate. Un argent radiochimiquement pur est finalement précipité et compté, sous forme d'iodate.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von Spuren von Silber in Galena und Blende durch Aktivierung mit Neutronen. Die radiochemische Trennung wurde nach Zugabe eines Trägers hauptsächlich durch Fällung des Silbers als Chlorid, Sulfid, Oxyd und Jodat vorgenommen. Radiochemisch reines Silber wurde zum Schluss gefällt und als Jodat ausgezählt; die chemische Ausbeute wurde gravimetrisch ermittelt.

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A SIMPLE METHOD FOR THE DETECTION OF SMALL AMOUNTS OF α-AMINO ACIDS

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INTRODUCTION

Copper salts react in alkaline media with α-amino acids to give water-soluble, blue diammino-diacid complexes[1]. This capacity to form complexes has been employed by POPE AND STEVENS[2] in their method for the quantitative determination of α-amino acids in body fluids and by CRUMPLER AND DENT[3] in distinguishing the α-amino acids from other amino acids.

In this paper, the dissolution of sediments of $Cu_3(PO_4)_2$ by α-amino acids is adapted to detect trace amounts of α-amino acids in a small volume of liquid in the range μl–ml by the impregnation method on blotting paper.

The principle of this method is based up on washing off the impregnating substance from the blotting paper and developing the background with rubeanic acid.

TECHNIQUE

Preparation of the impregnated blotting paper

Chromatographic or good blotting-paper strips (8 cm in width) can be impregnated with copper orthophosphate by dipping them into a copper chloride solution (0.3 g/l) and drying them after the excess of liquid is pressed out by a photographic roller. The strips are then dipped into sodium orthophosphate solution ($Na_3PO_4 \cdot 12\ H_2O$, concn. 1.5 g/l); Na^+ and Cl^- ions are removed from the blotting paper by washing in a current of distilled water. Good impregnated blotting paper can also be obtained by methods described by KIELCZEWSKI[4] or BUKATSCH AND WILDNER[5].

The detection procedure

Small quantities of the liquids are placed on the blotting paper by a self-filling ultramicro pipette[6], applying the glass apparatus for "ring" spot testing as constructed by BHUCHAR[7], or the apparatus for spotting analysed substances on the chromatograms as devised by ANTOSZEWSKI[8].

In order to put greater volumes of liquid on to the paper, (0.1 ml or more) the apparatus constructed by MAHR AND KLAMBERG[9,10] can be applied. The detection of α-amino acids in the powdered samples can be carried out by the method described by TÖPPEL[11], after which the investigated sample is placed in the capillary through which the water or buffer solution runs. The preparation should be mixed with powdered cellulose (1 : 1 v/v). To detect the α-amino acids in biological samples, one can make use of the micro-extractor constructed by ANTOSZEWSKI[12].

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A drop of the investigated solution buffered by borax buffer (1 : 1 v/v) (57.21 g $Na_2B_4O_7 \cdot 10\,H_2O$ + 1000 ml H_2O + 100 ml 1*N* HCl diluted to 2 l) is put on the impregnated paper, washed by a drop of distilled water, held over ammonia (2 min) and treated with, or dipped into a 0.1% ethanolic solution of rubeanic acid (dithiooxamid)[13]. The white fleck on the dark green, nearly black background indicates the presence of *a*-amino acids.

RESULTS

By the described method, 0.02–0.05 μg of *a*-amino acids can be detected. When the volume of the sample exceeds 0.1 ml, any small amount of impregnating substance can be washed out from the paper even by pure water; therefore, a control test should be carried out. Soluble peptides can also cause white flecks on the impregnated paper. This method permits the detection of the *a*-amino acids in the presence of small amounts of ammonia and considerable quantities of urea and salts. It seems possible to regain the *a*-amino acids for further research after having carried out other micro-preparative operations.

At present, a quantitative modification of this method for chromatographical purposes as well as its adaptation for ultramicro-methods (using isotope ^{32}P) for cytophysiological purposes, is being investigated.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to Professor Dr. W. Moycho, Department of Plant Physiology, University of Łódź, and Professor Dr. A. Lewandowski, Department of General Chemistry, University of Poznań, for their interest and helpful criticism of this work.

SUMMARY

A method for the detection of small amounts (0.02 μg or more) of *a*-amino acids on blotting paper impregnated by copper orthophosphate is described.

RÉSUMÉ

Une méthode est décrite pour déceler de faibles quantités d'acides aminés, en utilisant un papier imprégné de phosphate de cuivre.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zum Nachweis sehr kleiner Mengen *a*-Aminosäuren mit Hilfe von Filterpapier, das mit Kupferorthophosphat imprägniert ist.

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ANNOUNCEMENT

GORDON RESEARCH CONFERENCES

The Gordon Research Conferences for 1959 will be held from 15 June to 4 September at Colby Junior College, New London, New Hampshire; New Hampton School, New Hampton, New Hampshire and Kimball Union Academy, Meriden, New Hampshire.

Purpose. The conferences were established to stimulate research in universities, research foundations and industrial laboratories. This purpose is achieved by an informal type of meeting consisting of scheduled lectures and discussion groups. Sufficient time is available to stimulate informal discussions among the members of a conference. Meetings are held in the morning and in the evening, Monday through Friday, with the exception of Friday evening. The afternoons are available for recreation, reading or participation in discussion groups as the individual desires. This type of meeting is a valuable means of disseminating information and ideas to an extent that could not be achieved through the usual channels of publication and presentation at scientific meetings. In addition, scientists in related fields become acquainted, and valuable associations are formed that often result in collaboration and cooperative efforts between different laboratories.

It is hoped that each conference will extend the frontiers of science by fostering a free and informal exchange of ideas among persons actively interested in the subjects under discussion. The purpose of the program is not to review the known fields of chemistry and physics, but primarily to bring experts up to date on the latest developments, to analyze the significance of these developments, and to provoke suggestions concerning the underlying theories and profitable methods of approach for making new progress.

In order to protect individual rights and to promote discussion, it is an established requirement of each conference that no part of the information presented is to be used without specific authorization of the individual making the contribution, whether in formal presentation or in discussion. Scientific publications are not prepared as emanating from the conferences.

Attendance. Requests for attendance at the conferences, or for additional information should be addressed to W. GEORGE PARKS, Director, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island. From 15 June to 4 September 1959 mail should be addressed to Colby Junior College, New London, New Hampshire.

GORDON RESEARCH CONFERENCES

ANALYTICAL CHEMISTRY SECTION

17–21 August 1959
New Hampton School
New Hampton, New Hampshire

JOHN MITCHELL, JR., Chairman
CHARLES N. REILLEY, Vice Chairman

17 *August*

S. DAL NOGARE, Gas Chromatography.
R. F. GODDU, Near Infrared Spectroscopy.
L. C. JONES, JR., Far Ultraviolet Spectroscopy.

18 *August*

R. BELCHER, Elemental Analysis.
F. E. CRITCHFIELD, Functional Group Analysis.

19 *August*

L. GIERST, Galvanostatic and Potentiostatic Methods.
Open Discussion.

20 *August*

D. L. WOOD, Infrared Spectroscopic Methods for Characterizing High Polymers.
L. H. PHIFER, Decomposition of High Polymers.

21 *August*

R. J. KEIRS, Fluorescence and Phosphorescence.

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